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Inorganica Chimica Acta

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F. Albert Cotton, Carlos A. Murillo, Xiaoping Wang

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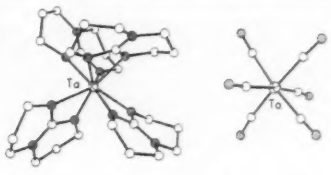
A compound containing two tantalum atoms in oxidation states separated by six units

The mixed-valent compound $[Ta(hpp)_4][Ta(CO)_6]$ has an eight-coordinate Ta(V) cation and a six-coordinate hexacarbonyltantalate(−I) anion.



Cynthia K. Schauer, Eric J. Voss, Michal Sabat, Duward F. Shriver

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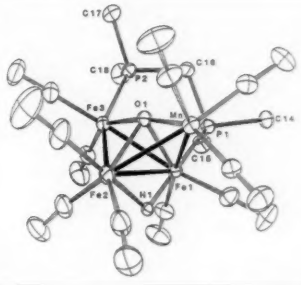
Proton reactivity of butterfly oxo and sulfido clusters and structural characterization of $HFe_3Mn(CO)_{10}(dmpm)(\mu_4\text{-}O)$

A new mixed-metal phosphine oxo system has been protonated, and shown to contain a butterfly arrangement of the metals with a hydrogen on the Fe–Fe backbone.



Benno Bildstein, Michael Malaun, Holger Kopacka, Marco Fontani, Piero Zanello

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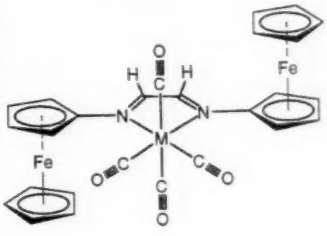
Synthesis and electrochemistry of ferrocenyldiazabutadiene metal carbonyl complexes (Fc-DAB)M$(CO)_4$ [M = Cr,Mo,W]

Ferrocenyldiazabutadiene carbonyl complexes of Cr(0), Mo(0), W(0) have been prepared, characterized, and their properties are compared to those of other analogous but non-ferrocenylated diazabutadiene complexes. Electrochemical measurements show ferrocene based, metal carbonyl localized, and ligand centered redox processes.



Kimberly J. Smith, Andrea L. Ondracek, Nadine E. Gruhn, Dennis L. Lichtenberger, Phillip E. Fanwick, Richard A. Walton

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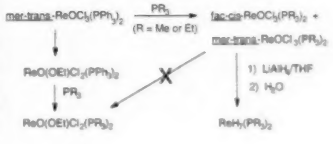
A comparative study of the isomers of $ReOCl_3(PMe_3)_2$ and $ReOCl_3(PEt_3)_2$. The isolation and characterization of $ReH_7(PR_3)_2$ and $ReO(OEt)Cl_2(PR_3)_2$ (R = Me or Et) and the photoelectron spectrum of $ReH_7(PMe_3)_2$

The reactions of *mer–trans*-$ReOCl_3(PPh_3)_2$ with PMe_3 and PEt_3 provide a route to the isomers *fac–cis*-$ReOCl_3(PR_3)_2$ and *mer–trans*-$ReOCl_3(PR_3)_2$ (R = Me or Et) which can be converted to $ReH_7(PR_3)_2$ (R = Me or Et) in ca. 60% yield by reaction with $LiAlH_4$ in THF and subsequent hydrolysis of the reaction mixtures.



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G. Chiericato Jr., C.R. Arana, C. Casado, I. Cuadrado, H.D. Abruña

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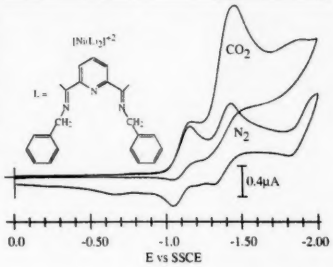
Electrocatalytic reduction of carbon dioxide mediated by transition metal complexes with terdentate ligands derived from diacetylpyridine

Fe, Co, and Ni complexes of terdentate ligands derived from diacetylpyridine exhibit electrocatalytic activity towards the reduction of carbon dioxide. The electrocatalytic activity, in terms of the diminution of the overpotential and increase in current, was dependent on both the metal center and the ligand.



Fernande D. Rochon, Robert Melanson, Pi-Chang Kong

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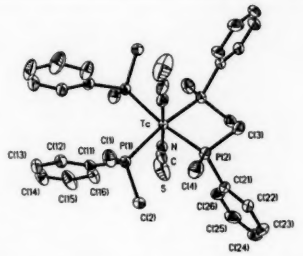
Synthesis of new mixed-ligands Tc complexes containing monodentate phosphine and isothiocyanato ligands. Crystal structures of complexes $Tc(P(C_3H_7)_3)_2(NCS)_4$, $Tc(P(CH_3)_2Ph)_4(NCS)_2$ and $Tc(P(OCH_3)Ph_2)_4(NCS)_2 \cdot 0.5CH_2Cl_2$

Three mixed-ligand neutral technetium complexes containing monodentate phosphine and isothiocyanato ligands were synthesized and studied by crystallographic methods. The crystal structures of *trans*-$Tc(P(C_3H_7)_3)_2(NCS)_4$, *trans*-$Tc(P(CH_3)_2Ph)_4(NCS)_2$, and *trans* - $Tc(P - (OCH_3)Ph_2)_4(NCS)_2 0.5CH_2Cl_2$, were determined. The isothiocyanato ligands are N-bonded to Tc. Important distortions of the octahedron were observed in the $P(CH_3)_2Ph$ compound, due to the bulkiness of the four ligands located in the same plane.



Edwin C. Constable, Catherine E. Housecroft, Markus Neuburger, Alain G. Schneider, Bernhard Springler, Margareta Zehnder

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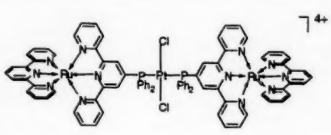
Programmed assembly of heteromultinuclear complexes using 4′-diphenylphosphino-2,2′:6′,2″-terpyridine

The complex $[Ru(tpy)(\mathbf{1})]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine; **1** = 4′-diphenylphosphino-2,2′:6′-,2″-terpyridine) reacts with *trans*-$[PdCl_2(NCMe)_2]$ to give *trans*-$[PdCl_2\{(\mu\text{-}\mathbf{1})Ru(tpy)\}_2]^{4+}$, and with *trans*-$[PtCl_2(NCPh)_2]$, to give *trans*-$[PtCl_2\{(\mu\text{-}\mathbf{1})Ru(tpy)\}_2]^{4+}$ which isomerizes in solution to the *cis*-isomer. Ligand **1** reacts with *trans*-$[PtCl_2(NCPh)_2]$ to yield *cis*-$[PtCl_2(\mathbf{1})_2]$, the structure of which has been determined for the monohydrate and for *cis*-$[PtCl_2(\mathbf{1})_2] \cdot CH_2Cl_2 \cdot 1.6C_5H_{12}$; significant differences in structure are observed dependent upon whether the solvate molecules are able to form hydrogen-bonded interactions with the complex.



Philip C. Andrews, Stacey M. Lawrence, Colin L. Raston, Brian W. Skelton, Vicki-Anne Tolhurst, Allan H. White

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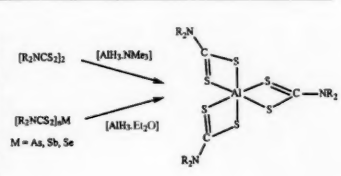
Dithiocarbamate complexes of trivalent aluminium and gallium via metal hydrides

Al(III) and Ga(III) dithiocarbamates, $[R_2NC(=S)S]_3M$, (R = Me, Et, Bz,), have been prepared by the reaction of the metal hydrides with the parent dithiurams and also by transmetallation with other metal dithiocarbamate complexes allowing their solid state structures to be investigated by single crystal X-ray diffraction and compared with the variety of metal dithiocarbamate structures available in the literature.



Anne M. Wilson, F.G. West, Arnold L. Rheingold, Richard D. Ernst

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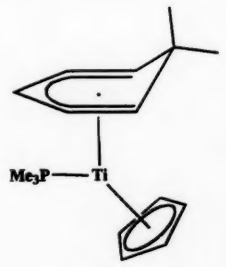
Synthesis, characterization, and organic chemistry of an edge-bridged half-open titanocene

Ti (C_5H_5) (6,6 - dimethylcyclohexadienyl) (P-Me_3) has been synthesized and characterized. The Ti–C bonds for the dmch ligand are much shorter than those for the Cp ligand, reflecting stronger metal binding for dmch. The dmch ligand is still more reactive, engaging in coupling reactions with ketones. With two ketone equivalents, unusual 1,4 regiochemistry results which can be explained mechanistically.



John A. Bellefeuille, Craig A. Grapperhaus, Agnes Derecskei-Kovacs, Joseph H. Reibenspies, Marcetta Y. Darensbourg

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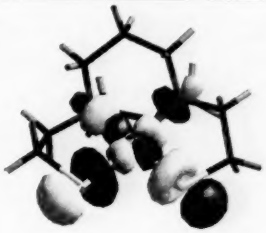
Correlation of electrochemistry, nucleophilicity and density functional calculations of the *cis*-dithiolate (bme*-daco)Ni

DFT calculations correlate the accessability of Ni(II/I) redox couples in N_2S_2 complexes with nickel-based LUMO energies.



Vivian Wing-Wah Yam, Alex Sze-Fai Kai

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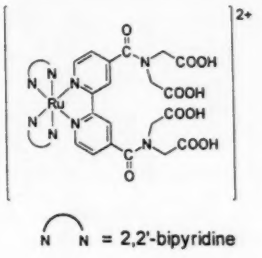
Luminescence cation sensing by ruthenium(II) complexes containing an iminodiacetic acid-appended ligand

A series of ruthenium(II) polypyridine complexes with iminodiacetic acid-containing ligand have been synthesized and characterized. The photophysical properties of the complexes at different pH were studied. The cation-binding properties of these complexes for lanthanide ions have been studied by electronic absorption spectroscopy, emission and cyclic voltammetry. The binding constants K_s for europium(III) and lanthanum(III) ions have been determined.



Chun-An Chen, Lin Chi-Hung, J.A. Cowan

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Functional role of a conserved tryptophan residue of *Chromatium vinosum* high potential iron protein

A Trp80Asn mutant of *Chromatium vinosum* HiPIP shows a minimal change both in E_M for the $[Fe_4S_4]^{3+/2+}$ cluster (+33 mV) and in electron transfer properties. The reduced state is stable in an aerobic environment, but displays a more pronounced temperature-dependent degradation that is mediated by unfolding of the protein prior to degradation of the cluster.

Andre Morneau, Bernadette T. Donovan-Merkert, William E. Geiger

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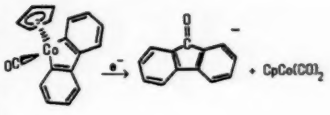
An electron-transfer induced migratory insertion reaction originating from a 19-electron cobaltacyclic anion

The cobaltacycle shown is reduced in THF in a one-electron irreversible process yielding two non-trivial (besides CO) products: $CpCo(CO)_2$ and the fluorenone anion radical. The latter is proposed to arise from the migratory insertion of the CO ligand into the metallacyclic Co–C bond in the putative 19-electron complex. An equilibrium between 19- and 17-electron complexes accounts for the observed products.

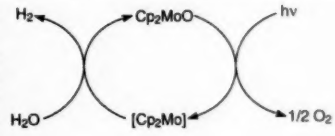


Gregory T. Baxley, Alfred A. Avey, Tim M. Aukett, David R. Tyler

Inorg. Chim. Acta 300–302 (2000) 102

Photoactivation of water by Cp'_2Mo and photochemical studies of Cp_2MoO. Investigation of a proposed water-splitting cycle and preparation of a water-soluble molybdocene dihydride

The photochemistry of Cp_2MoO is consistent with the intermediate formation of Cp_2Mo, a result that suggests O_2 may also be forming in these reactions and that Cp_2MoO may be useful as a catalyst for photochemical water-splitting. However, gas chromatographic, mass spectroscopic, and chemical analyses showed that free O_2 was not a product. It is concluded that if O_2 is produced by irradiation of Cp_2MoO, it is either at a level below our detection limits (as low as 0.02 μmol of O_2) or it is reacting too rapidly with Cp_2MoO to be detected.



Thomas R. Cundari, Wentao Fu

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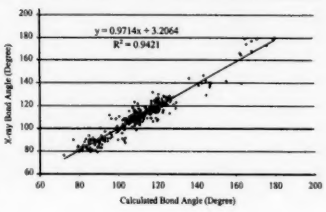
Genetic algorithm optimization of a molecular mechanics force field for technetium

A new force field was developed using genetic algorithms (GAs) to optimize molecular mechanics (MM) parameters. The GA-MM approach was applied to the study of technetium (Tc) complexes with coordination numbers of 5 or 6 and metal oxidation states of +3 to +6. Soft and hard donor ligands were studied. Good modeling was achieved in a fraction of the time of quantum methods, with considerably less computational resources.



Thomas Scheiring, Wolfgang Kaim, José A. Olabe, Alejandro R. Parise, Jan Fiedler

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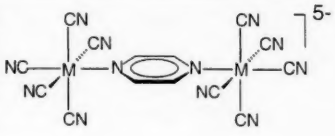
The valence-localized decacyanodiruthenium(III,II) analogue of the Creutz–Taube ion. Completing the full d^5/d^6 triad $[(NC)_5M(\mu\text{-pz})M(CN)_5]^{5-}$, M = Fe,Ru,Os; pz = pyrazine

The missing diruthenium(II,III) compound in the series of pyrazine-bridged mixed-valent decacyanodimetal(II,III) complexes was characterized by UV–Vis/IR spectroelectrochemistry. In comparison to the Fe and Os analogues and to the decaammine diruthenium(II,III) species (i.e. the Creutz–Taube ion) the new d^5/d^6 system exhibits rather weak metal–metal coupling, as indicated by $K_c = 10^{4.7}$ (in CH_2Cl_2) and agreement with the Hush model for inter-valence charge transfer.



A. Antiñolo, F. Carrillo-Hermosilla, J. Fernández-Baeza, A.M. Fernández de Toro, S. García-Yuste, A. Otero, J.C. Pérez-Flores, A.M. Rodríguez

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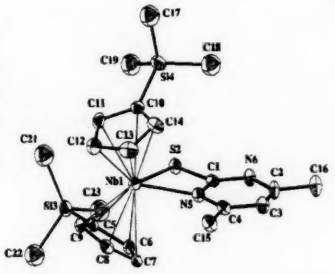
Synthesis and characterization of thiolate, -amido, and -oxy heterocyclic-containing niobocene complexes: X-ray molecular studies of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}N,S\text{-}S(C_6H_7N_2))]$ **(3)**

The thermal treatment of the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(H)_3]$ with the corresponding mercapto-, hydroxy-, amino-pyrimidine or -pyrimidine affords thiolate-, oxy-, amido-pyridine and -pyrimidine-containing niobocene derivatives. An X-ray diffraction study has been carried out for complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}N,S\text{-}S(C_6H_7N_2))]$ **(3)**.



Anthony D. Selmeczy, William D. Jones

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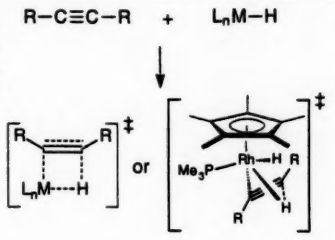
Insertions of electrophiles into metal hydride bonds. Reactions of $(C_5Me_5)Rh(PMe_3)H_2$ with activated alkynes to produce η^2-alkene complexes

The reactions of $(C_5Me_5)Rh(PMe_3)H_2$ with alkynes lead to η^2-olefin complexes by way of vinyl hydride intermediates. The mechanism and stereochemistry of these reactions are discussed.



Anne Dolbecq, Emmanuel Cadot, Dirk Eisner, Francis Sécheresse

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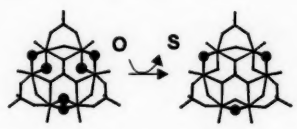
Regioselective S/O substitutions in heteropolyoxothioanions: ^{31}P NMR study and X-ray crystal structure of the half-substituted anion $[(HPO_4)_4Mo_6S_3O_9(OH)_3]^{5-}$

The $[(HPO_4)_4Mo_6S_3O_9(OH)_3]^{5-}$ anion is built from the association of three $\{Mo_2SO_3\}$ dinuclear units, connected to each other by phosphate groups. This anion is obtained from the sulfurated parent $[(HPO_4)_4Mo_6S_6O_6(OH)_3]^{5-}$ through regioselective S/O substitution reactions. Only the three sulfur bridging atoms in the opposite side to the peripheral PO_4 groups are substituted by oxygen atoms.



Edwin C. Constable, Oliver Eich, Catherine E. Housecroft, David C. Rees

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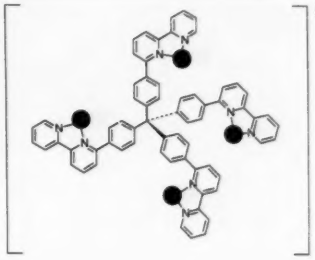
Metallostars containing $\{Ru(bpy)_3\}$ motifs

A pair of ligands in which three or four 2,2′-bipyridine (bpy) metal-binding domains are sited about a central core have been prepared. In the case of a ligand bearing four bpy units attached to the *para*-positions of a central tetraphenylmethane core, the tetranuclear complex containing four $\{Ru(bpy)_3\}$ units has been prepared and shown to consist of a mixture of diastereomers.



Bernd Wrackmeyer, Oleg L. Tok, Elena Klimkina, Yuri N. Bubnov

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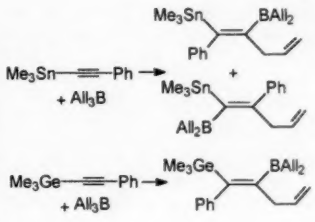
Reactivity of mono-1-alkynyltin and -germanium compounds towards triallylborane

1-Alkynyltin and 1-alkynylgermanium compounds $R_3M–C{\equiv}CR^1$ react with triallylborane, All_3B, preferably by stereoselective 1,1-allylboration. Only in the case of $Me_3Sn–C{\equiv}CPh$ the 1,2-allylboration product is formed in an appreciable amount. If R^1 is bulky (e.g. ^{t}Bu, $SiMe_3$, $SnMe_3$) alkynyl/allyl exchange is an alternative reaction. A smooth and quantitative 1,1-allylboration takes place with $Bu_3Sn–C{\equiv}CFc$, $Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$, providing an easy access to alkenes bearing the ferrocenyl and the stannyl group in geminal positions.



Joseph P. al Dulaimi, Robin J.H. Clark, Marcia Saavedra S., Md. Abdus Salam

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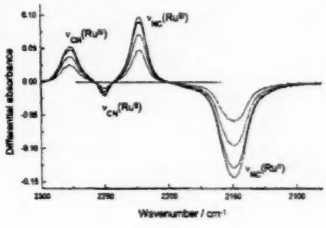
Spectroelectrochemical studies on some new ruthenium(II) complexes containing both cyanide and isocyanide ligands

The first mixed cyanide/isocyanide complexes of ruthenium(II) and, by electrochemical generation, of their ruthenium(III) counterparts have been synthesised. All of the ruthenium(II) and ruthenium(III) species have been shown by infrared spectroscopy (IR-RAS) to have the *trans-trans-trans*-octahedral geometry.



B. Müller, H. Vahrenkamp

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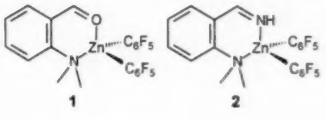
A zinc–aldimine complex

The title complex dimethylaminobenzaldimine – zinc - bis(pentafluorothiophenolate) was obtained from the reaction of dimethylaminobenzaldehyde with ammonia-contaminated zinc-bis(pentafluorothiophenolate). Zinc effects the catalytic formation and stabilization of the aldimine by complexation. This is the first case where the molecular structures of the corresponding aldehyde and aldimine complexes could be compared.



Mauro C.M. Laranjeira, Rosemary A. Marusak, A. Graham Lappin

Inorg. Chim. Acta 300–302 (2000) 186

Driving force effects in proton coupled electron transfer

Reduction of $[Ni^{III}(Me_2L)]^+$ by $[Fe^{II}(Me_2LH)]^+$, where the ligand, Me_2LH_2, is 3,14 - dimethyl - 4,7,10,13 - tetraazahexadeca-3,13-diene-2,15-dione dioxime leads to products $[Ni^{II}(Me_2LH)]^+$ and $[Fe^{III}(Me_2L)]^+$ where proton transfer has accompanied electron transfer. The rate of this process is almost three orders of magnitude faster than expected for electron transfer alone, suggesting that the acceleration results from a coupling of the electron and proton transfer steps.

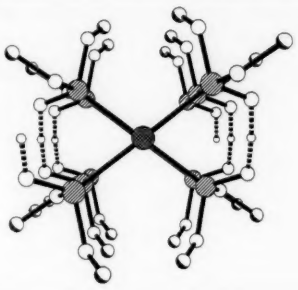
$$[Ni^{III}(Me_2L)]^+ + [Fe^{II}(Me_2LH)]^+ \longrightarrow [Ni^{II}(Me_2LH)]^+ + [Fe^{III}(Me_2L)]^+$$

Christian Hollatz, Annette Schier, Hubert Schmidbaur

Inorg. Chim. Acta 300–302 (2000) 191

Gold(I) complexes with P=O and P–OH functionalised phosphorus ligands

Gold(I) complexes with phosphorous or diorganylphosphorous acid as ligands form oligomeric aggregates with hydrogen bonds supporting the gold–gold bonded pairs or strings of monomers. Phosphite complexes oligomerise solely via aurophilic bonding.

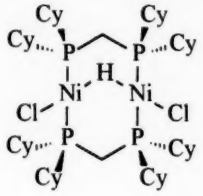


Charles E. Kriley, C. Joy Woolley, Matthew K. Krepps, Eric M. Popa, Phillip E. Fanwick, Ian P. Rothwell

Inorg. Chim. Acta 300–302 (2000) 200

Synthesis and characterization of a series of novel nickel(II)/nickel(I) complexes. Crystal structures of $[NiCl_2(dcpm)]$, $[Ni(dcpm)_2](NO_3)_2{\cdot}2EtOH$, $[Ni_2Cl_2(\mu dcpm)_2(\mu\text{-}H)]$ and $[Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2]$; dcpm = bis(dicyclohexylphosphino)methane

The complexes $[(dcpm)NiCl_2]$ (**1**), $[Ni_2Cl_2(\mu\text{-}dcpm)_2(\mu\text{-}H)]$ (**3**), $[Ni_2(\mu\text{-}PCy_2)_2(PCy_2Me)_2]$ (**4**) and $[Ni(dcpm)_2](NO_3)_2{\cdot}2EtOH$ (**2**), dcpm = bis(dicyclohexylphosphino)methane, have been prepared and characterized by ^{31}P, ^1H NMR (or EPR) as well as X-ray crystallography. The salt $NiCl_2{\cdot}6H_2O$ was found to react with dcpm to form the monomeric, four coordinate, diamagnetic complex $[(dcpm)NiCl_2]$ (**1**). Complex **1** was then reduced with Bu^n_3SnH (or LiH with heating) in toluene at room temperature to form the air sensitive 'A-frame' complex $[Ni_2Cl_2(\mu\text{-}dcpm)_2(\mu\text{-}H)]$ (**3**). The Ni–Ni bond distance for **3** was found to be 2.904(3) Å showing the lack of any Ni–Ni metal bonding.

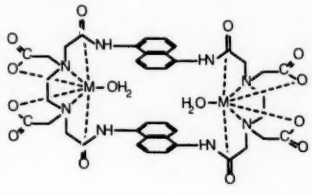


Michiko B. Inoue, Iliana C. Muñoz, Motomichi Inoue, Quintus Fernando

Inorg. Chim. Acta 300–302 (2000) 206

X-ray structures and fluorescence spectra of binuclear Zn^{2+} and Cd^{2+} complexes of an amide-based naphthalenophane

A chelating amide-based naphthalenophane forms binuclear Zn^{2+} and Cd^{2+} complexes. The ligand molecule has a high steric constraint, and metal complexation causes structural deformation of the naphthyl groups as a result of contraction of the macrocyclic ring. The unique structural features lead to novel fluorescence properties including intensity changes with pH and with metal complexation.

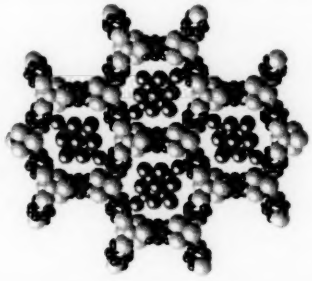


Douglas Hagrman, Pamela Hagrman, Jon Zubieta

Inorg. Chim. Acta 300–302 (2000) 212

Polyoxomolybdate clusters and copper–organo-nitrogen complexes as building blocks for the construction of composite solids

The reactions of MoO_3 and $CuSO_4{\cdot}5H_2O$ with a variety of nitrogen donor ligands under hydrothermal conditions yield organic–inorganic composite materials constructed from polyoxomolybdate clusters and copper-ligand coordination complex cations. Both the organic component and the secondary metal coordination preferences may have profound influences on the oxide microstructure.

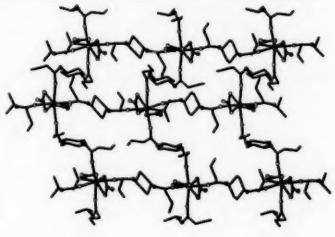


David M.L. Goodgame, David A. Grachvogel, Izhar Hussain, David J. Williams

Inorg. Chim. Acta 300–302 (2000) 225

Polymeric lanthanide complexes with extended reach bisamide ligands

A number of lanthanide complexes with the bisamide ligands *N,N'-p*-xylylenebisacetamide, *N,N'-trans*-1,4-cyclohexylaminebisacetamide, *N,N'-trans*-1,4-cyclohexylaminebis-*n*-butyramide have been prepared and three representative examples have been structurally characterised by X-ray diffraction methods. The bisamide ligands bridge the metal centres so as to form polymeric sheet structures containing contiguous large (44- or 78-membered) rings.

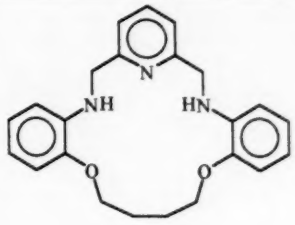


Laura Valencia, Harry Adams, Rufina Bastida, Andres de Blas, David E. Fenton, Alejandro Macías, Adolfo Rodríguez, Teresa Rodríguez-Blas

Inorg. Chim. Acta 300–302 (2000) 234

Synthesis and characterization of cobalt, nickel, zinc and cadmium compounds with a pyridine-derived N_3O_2 macrocycle: Crystal and molecular structures of the macrocyclic ligand and Co(II), Ni(II) and Zn(II) complexes

The interaction of Co(II), Ni(II) and Cd(II) nitrates and perchlorates with the 17-membered pyridine-derived macrocycle containing an N_3O_2-donor set has been investigated. The oxaazamacrocyclic ligand L and the metal complexes have been fully characterized by conventional spectroscopic techniques, and the X-ray crystal structures of the macrocycle L and of the complexes $[CoL](NO_3)_2$, $[NiL](NO_3)_2$ and $[ZnL(H_2O)(CH_3CN)](ClO_4)_2$ have been determined.



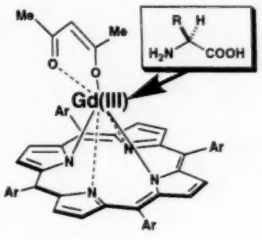
L

Hitoshi Tamiaki, Natsushi Matsumoto, Satomi Unno, Satoshi Shinoda, Hiroshi Tsukube

Inorg. Chim. Acta 300–302 (2000) 243

Induced circular dichroism active complexes of synthetic gadolinium(III) porphyrinates with chiral amino acids

Synthetic gadolinium(III) *meso*-tetraarylporphyrinates extracted zwitterionic L-amino acid from an aqueous solution to give a 1:1 complex in benzene or dichloromethane through synergistic binding of both the amino and carboxylic groups. The resulting highly coordinated complex afforded chirality-dependent, intense circular dichroism bands of reversed S-shape type at the Soret region (400–450 nm).



Gregory J. Grant, Myron W. Jones, Kristi D. Loveday, Donald G. VanDerveer, William T. Pennington, Cassandra T. Eagle, Larry F. Mehne

Inorg. Chim. Acta 300–302 (2000) 250

Transition metal complexes with macrocyclic oxathiaethers

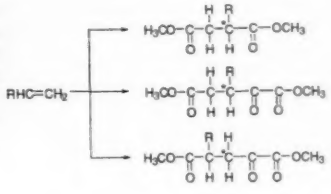
Complexation studies with Ni(II), Co(III), Co(II), Cd(II), and Cu(II) for the two mixed oxathia crown ligands $9S_2O$ and $18S_4O_2$ are reported. The copper(II) complex, $[Cu(9S_2O)_2](BF_4)_2$, shows an interesting Jahn-Teller distortion resulting in all of the coordinate bonds being remarkably similar in length. In all of these complexes, the two oxathiaether ligands function as much weaker field ligands than do their crown thioether analogs.

Martin Sperrle, Giambattista Consiglio

Inorg. Chim. Acta 300–302 (2000) 264

Palladium-catalyzed enantioselective multiple carbonylation of 1-olefins. Synthesis of optically active 2-oxo-pentanedioates and butanedioates

Optically active 2-oxopentanedioates and butanedioates are accessible through multiple carbonylation reactions of 1-olefins catalyzed by cationic palladium(II) complexes modified with chiral diphosphines. Chemo-, regio- and enantioselectivity results point towards common intermediates for the two reactions.

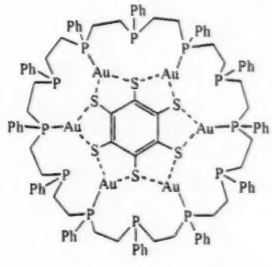


Jennifer A. Harnisch, Robert J. Angelici

Inorg. Chim. Acta 300–302 (2000) 273

Gold and platinum benzenehexathiolate complexes as large templates for the synthesis of 12-coordinate polyphosphine macrocycles

A conceptually new strategy for the synthesis of large-ring, poly-donor macrocycles using multi-metal ion templates is illustrated by the synthesis of a 36-membered macrocycle containing 12 phosphorus donors constructed on a template ($C_6S_6Au_6$) consisting of benzenehexathiolate coordinated to six Au^+ ions

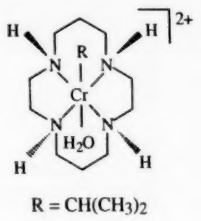


Andreja Bakac, Vjera Butkovic, James H. Espenson, Matko Orhanovic

Inorg. Chim. Acta 300–302 (2000) 280

Concurrent homolysis, β-elimination, and hydrolysis of macrocyclic alkylchromium complexes

The complex *trans*-$L^1(H_2O)CrCH(CH_3)_2^{2+}$ undergoes three parallel first order reactions — homolysis ($k = 0.003\ s^{-1}$), hydrolysis ($k \sim 2.5 \times 10^{-5}\ s^{-1}$), and β-elimination ($k \sim 1.9 \times 10^{-5}\ s^{-1}$).



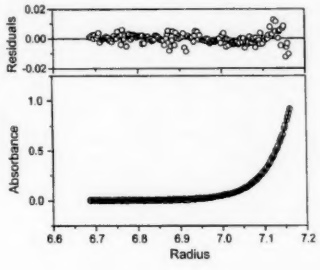
R = $CH(CH_3)_2$

Kenji Nomiya, Yukinori Arai, Yasushi Shimizu, Mizuto Takahashi, Toshio Takayama, Heiko Weiner, Toshi Nagata, Jason A. Widegren, Richard G. Finke

Inorg. Chim. Acta 300–302 (2000) 285

Synthesis and characterization of the tetrameric, tri-titanium(IV)-substituted Wells–Dawson-substructure polyoxotungstate, $[(P_2W_{15}Ti_3O_{60.5})_4]^{36-}$: the significance of ultracentrifugation molecular weight measurements in detecting aggregated, anhydride forms of polyoxoanions

The preparation and characterization of various salts of a tri-Ti^{IV}-substituted Wells–Dawson-substructure polyoxoanion are described. Ultracentrifugation solution molecular weight (MW) experiments show that this polyoxoanion exists in aggregated, Ti–O–Ti anhydride forms, thereby illustrating the importance of MW data in the correct formulation of polyoxoanions that can form anhydride bonds.

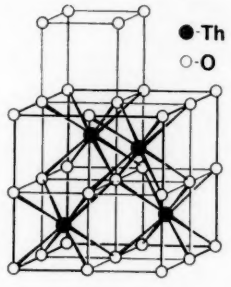


Trevor R. Griffiths, James Dixon

Inorg. Chim. Acta 300–302 (2000) 305

Electron irradiation of single crystal thorium dioxide and electron transfer reactions

Electron irradiation turns single crystals of thoria blue. 3 MeV electrons transferred sufficient energy to displace lattice oxygen atoms, but not thorium atoms. The spectrum of the blue colour was similar, but not identical, to that generated with neutron irradiation. Defects created here are of shallow energy and intervalence bands only occurred in the presence of aggregates of impurity ions.

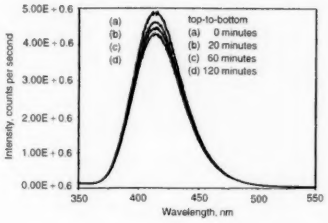


Nattapong Srisook, Joseph Rizzolo, George E. Shankle, Howard H. Patterson

Inorg. Chim. Acta 300–302 (2000) 314

Light-induced electron transfer in $Tl[Ag(CN)_2]$: Photochemical reaction of luminescent metal–metal exciplexes in the solid state

A single crystal of $Tl[Ag(CN)_2]$ shows 'optical memory'. That is, the luminescence spectrum is dependent on the irradiation history of the crystal. A light-induced electron transfer mechanism is proposed.

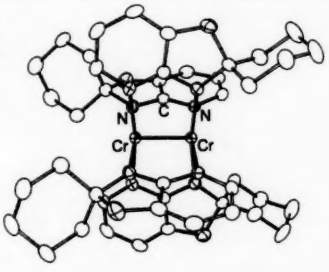


F. Albert Cotton, Lee M. Daniels, Carlos A. Murillo, Hong-Cai Zhou

Inorg. Chim. Acta 300–302 (2000) 319

The effect of divergent-bite ligands on metal–metal bond distances in some paddlewheel complexes

$Cr_2(CHIP)_4$, where CHIP is the anion of 1′, 3′ - dihydrospiro[cyclohexane - 1,2′ - [2*H*]-imidazo[4,5-*b*]pyridine], has been synthesized and crystallographically characterized. It has a Cr–Cr distance of 2.016(1) Å.

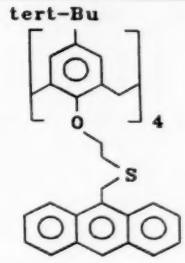


Stephan Knoblauch, O. Matthew Falana, Jaewook Nam, D. Max Roundhill, Horst Hennig, Kornelia Zeckert

Inorg. Chim. Acta 300–302 (2000) 328

Calix[4]arenes with narrow rim 2-mercaptoethoxy substituents as potential precursor molecules for metallacages and sensors

The compound 5,11,17,23-*tert*-butyl-25, 26,27,28-(2-mercaptoethoxy) calix[4]arene reacts with methylmercuric acetate to give 5,11,17,23-*tert*-butyl-25,26,27,28-(2-mercaptoethoxy mercuriomethyl) calix[4]arene. Sequential loss of dimethylmercury gives the cluster bis-(5,11,17,23-*tert*-butyl-25,26,27,28-(2-mercaptoethoxy)) tetramercury calix[4]-arene. 5,11,17,23-*Tert*-butyl-25,26,27,28-(2-mercaptoethoxy) calix[4]arene reacts with 9-chloromethyl-anthracene to give 5,11,17,23-*tert*-butyl-25,26,27,28-(9-thiomethylanthracylethoxy) calix[4]arene.



Eric S. Meadows, Leonard J. Barbour, Frank R. Fronczek, Cheri M. Evans, Steven F. Watkins, George W. Gokel

Inorg. Chim. Acta 300–302 (2000) 333

Channel-like structures formed from extended networks of 4,13-diaza-18-crown-6 complexes

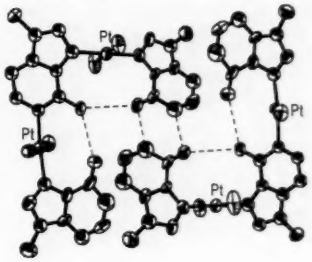
Solid state structures of complexes formed between sodium cation, water, and/or 4,13-diaza-18-crown-6 (**1**) are reported. The oxygen donor atoms of either water or the crown participate in forming a channel-like network of sodium cations that may emulate the interior of a channel's pore.

Irene B. Rother, Eva Freisinger, Andrea Erxleben, Bernhard Lippert

Inorg. Chim. Acta 300–302 (2000) 339

trans-$a_2Pt(II)$– (a = NH_3, CH_3NH_2) modified purine base pairs and triples: Hydrogen bonding between self-complementary pairs and triples and heterometal (Ag^+) coordination leading to a 1 D helix

trans-$a_2Pt(II)$– (a = NH_3, CH_3NH_2) modified purine base pairs and triples: Hydrogen bonding between self-complementary pairs and triples and heterometal (Ag^+) coordination leading to a 1 D helix. Purine model nucleobases cross-linked by *trans*-$a_2Pt(II)$ to 'metal-modified' base pairs and triples have been studied with regard to self-complementary H bonding and heterometal binding.

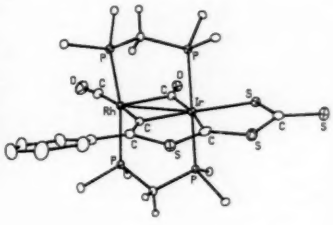


Darren S.A. George, Robert W. Hilts, Robert McDonald, Martin Cowie

Inorg. Chim. Acta 300–302 (2000) 353

Sulfur–carbon bond formation and bond cleavage in alkynyl-bridged heterobinuclear complexes of rhodium and iridium

The phenylacetylide-bridged heterobinuclear complex$[RhIr(CO)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_2Ph)(dppm)_2]^+$ reacts with CS_2 and SCN^nBu at $-80°C$ yielding analogous π adducts. Upon warming, the CS_2 adduct reacts further giving two C_2S_4-containing products, one of which has the C_2S_4 moiety sulfur-bound to the acetylide β-carbon, whereas the SCN^nBu adduct yields a sulfide-bridged, isocyanide product by S–C bond cleavage.

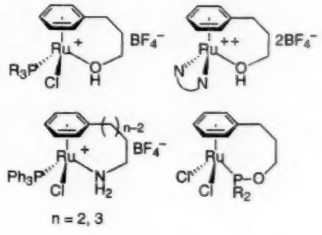


Yoshiharu Miyaki, Takafumi Onishi, Hideo Kurosawa

Inorg. Chim. Acta 300–302 (2000) 369

Synthesis and reaction of ruthenium(II) complexes containing heteroatom donor (O, N, and P) tethered to η^6-arene ring

Synthesis of ruthenium(II) complexes chelated by the η^6-arene ring and a pendent donor atom (O, N, and P) is described. Some alcohol chelate complexes were converted to alkoxide complexes by treatment with bases. In CH_2Cl_2 acidity of the hydroxy proton in the alcohol chelate complex was revealed to be comparable to that of *N*-methylbenzylammonium cation (pK_a in H_2O, ca. 11).

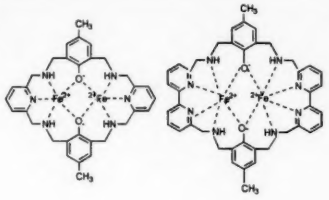


Zheng Wang, Arthur E. Martell, R.J. Motekaitis, J.H. Reibenspies

Inorg. Chim. Acta 300–302 (2000) 378

Dinuclear Fe(II) macrocyclic complexes as catalysts for the oxidation of hydrocarbons by molecular oxygen

The dinuclear ferrous complexes of two macrocyclic ligands have been found to catalyze the hydroxylation of cyclohexane and adamatane.

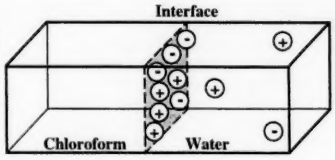


Frédéric Berny, Rachel Schurhammer, Georges Wipff

Inorg. Chim. Acta 300–302 (2000) 384

Distribution of hydrophilic, amphiphilic and hydrophobic ions at a liquid/liquid interface: a molecular dynamics investigation

Based on Molecular Dynamics simulations, the distribution of salts of 'symmetrical' hard (K^+, Na^+, Cl^-) or soft (SCN^-, Pic^-, $AsPh_4^+$, BPh_4^-) ions and of amphiphilic (phospholipid; ammonium) ions is described at a water/'oil' interface, showing contrasted behaviours and counterion effects. Implications for assisted ion extraction and electrochemistry are discussed.

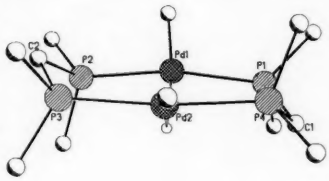


Robert A. Stockland Jr., Gordon K. Anderson, Nigam P. Rath

Inorg. Chim. Acta 300–302 (2000) 395

Synthesis and structures of hydride-bridged palladium A-frame complexes

The hydride-bridged palladium complexes $[Pd_2R_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ have been prepared from $[Pd_2Cl_2(\mu\text{-}dppm)_2]$ and RMgX, followed by CBr_4, $NaBH_4$ and $TlPF_6$. The unsymmetrical species $[PdPtR_2(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$ was generated analogously from $[PdPtCl_2(\mu\text{-}dppm)_2]$, whereas reaction of $[Pd(Mes)(dppm)_2]X$ with $[Pd_2R_2(\mu\text{-}Cl)(AsPh_3)_2]$, followed by treatment with $NaBH_4$, gave $[Pd_2(Mes)R(\mu\text{-}H)(\mu\text{-}dppm)_2]PF_6$. The complexes were characterized by elemental analysis, ^1H and ^{31}P NMR spectroscopy and, in several cases, by X-ray crystallography.

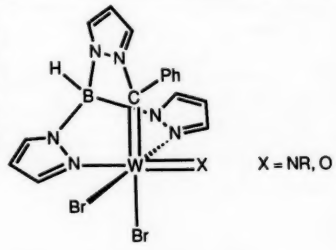


Andreas Mayr, Samyoung Ahn

Inorg. Chim. Acta 300–302 (2000) 406

Oxidatively induced insertion of an alkylidyne unit into the tungsten tris(pyrazolyl)borate cage

The oxidation of alkylidene tris(pyrazolate)borate tungsten complexes of the type $W(CHPh)(X)(BHPz_3)(Br)$ (X = imido or oxo) with bromine has been investigated with the objective of observing a coupling process of the metal–carbon multiple bond. Under the applied reaction conditions, the CPh group was found to insert into the tris-pyrazolyborate cage.

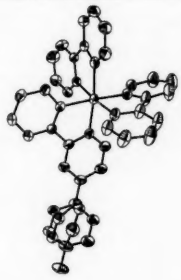


Yibing Shen, Keith A. Walters, Khalil Abboud, Kirk S. Schanze

Inorg. Chim. Acta 300–302 (2000) 414

Intramolecular charge transfer in pyridinium-substituted Ru-polypyridine complexes

A photophysical study has been carried out on the new pyridinium-substituted complex $(bpy)_2Ru(bpy\text{-}py\text{-}Me^+)^{3+}$. Temperature-dependent luminescence and transient absorption studies indicate that at temperatures ranging from 80 to 300 K the photophysics of $(bpy)_2Ru(bpy\text{-}py\text{-}Me^+)^{3+}$ is dominated by a low-lying $Ru \rightarrow bpy\text{-}py\text{-}Me^+$ MLCT state.

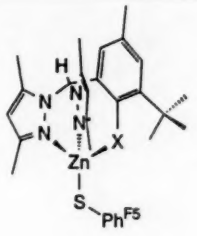


Brian S. Hammes, Carl J. Carrano

Inorg. Chim. Acta 300–302 (2000) 427

The structure and characterization of zinc heteroscorpionate complexes containing pentafluorothiophenol

A series of zinc heteroscorpionate complexes (L1OH and L2SH) containing pentafluorothiophenol have been synthesized and characterized. The results indicate that simply varying one donor atom from O to S in the tridentate ligands $(L1O)^-$ and $(L2S)^-$ can have an effect on the products formed at a pseudotetrahedral Zn(II) center.



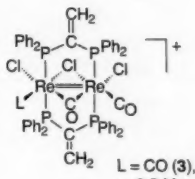
X = O or S

Shan-Ming Kuang, Phillip E. Fanwick, Richard A. Walton

Inorg. Chim. Acta 300–302 (2000) 434

Dirhenium complexes that contain the ligand 1,1-bis(diphenylphosphino)ethene (dppE). Synthesis, characterization and reactivity of $Re_2Cl_4(\mu\text{-dppE})_2$

The triply bonded dirhenium(II) complex $Re_2Cl_4(\mu\text{-dppE})_2$ (**1**) (dppE represents $(Ph_2P)_2C{=}CH_2$) has been synthesized and its properties and reactivity examined. Reaction with CO affords $Re_2Cl_4(\mu\text{-dppE})_2(CO)_2$ (**2**) which has in turn been converted to $[Re_2Cl_3(\mu\text{-dppE})_2(CO)_2(L)]\text{-}O_3SCF_3$, (L = CO (**3**), XylNC (**4**) or 2,5-Me_2–C_6H_3CN (**5**)). The complex *trans*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppE})_2$ (**6**) has been prepared from the reaction of $Re_2(\mu\text{-}O_2CCH_3)_4Cl_2$ with dppE. Compounds **1**, **2**, **4** and **6** have been characterized by X-ray crystallography.



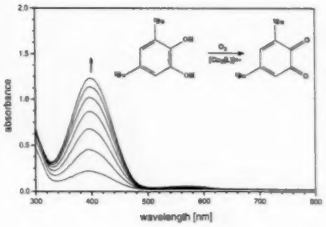
L = CO (**3**), XylNC (**4**) or 2,5-Me_2-C_6H_3CN (**5**)

Pavel Gentschev, Niclas Möller, Bernt Krebs

Inorg. Chim. Acta 300–302 (2000) 442

New functional models for catechol oxidases

Four new dinuclear copper(II) complexes were prepared exhibiting different coordination spheres with N_4O, N_3O_2 or N_2O_2 donor sets and different bridging systems. The Cu···Cu distances vary from 2.918(2) to 4.756(2) Å. The catalytic performance of the oxidation of 3,5-di-*tert*-butylcatechol to quinone was studied using UV–Vis absorption spectra methods.

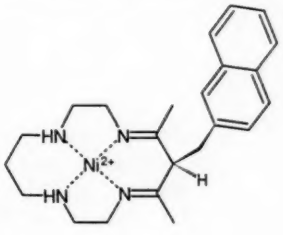


Luigi Fabbrizzi, Maurizio Licchelli, Chiara Rospo, Donatella Sacchi, Michele Zema

Inorg. Chim. Acta 300–302 (2000) 453

Searching for new fluorescence switches: naphthalene-containing metal complexes whose emission can be controlled by pH variations

A novel naphthalene-containing Ni(II) macrocyclic complex has been synthesized and structurally characterized. It undergoes a deprotonation at moderately basic pH values ($pK_a = 8.8$ in 4:1 MeCH–water solution). As the deprotonated species is distinctly less emissive, the fluorescence of the Ni(II) complex is quenched by addition of a base and revived by addition of an acid. Thus, a reversible variation of the emission intensity can be obtained simply by varying the pH of the solution.

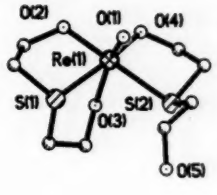


Frank J. Femia, John W. Babich, Jon Zubieta

Inorg. Chim. Acta 300–302 (2000) 462

Structural systematics of the $\{ReO\}^{3+}$ core with '3 + 2' ligand donor sets

The reaction of $[ReOCl_3(PPh_3)_2]$ with a series of tridentate and bidentate ligands has provided a facile route for the synthesis of a vast class of compounds with a '3+2' ligand composition about the $\{Re(V)O\}^{3+}$ core. The structural prototype for the series is [ReO{$(OCH_2CH_2)_2S$} {$OCH_2CH_2SCH_2CH_2OH$}] (**1**), where as compounds **2**–**5** are variants of the type [ReO{$(OCH_2CH_2)_2S$}{S ^ N}] where (S ^ N) is a mercaptopyridine or mercaptopyrimidine bidentate ligand. Likewise, compounds **6**–**17** are of the type [ReO{$(OCH_2CH_2)_2NR$}{S ^ N}] with the same series of bidentate ligands and R = $-CH_3$, $-CH_2CH_3$, $-(CH_2)_3CH_3$, and $-C(CH_3)_3$.

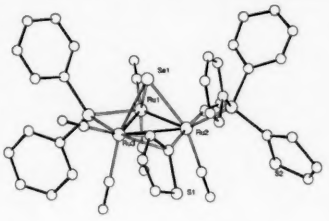


Daniele Cauzzi, Claudia Graiff, Chiara Massera, Giovanni Predieri, Antonio Tiripicchio

Inorg. Chim. Acta 300–302 (2000) 471

Multiple oxidative addition of diphenyl-2-thienylphosphine selenide to $[Ru_3(CO)_{12}]$: crystal and molecular structure of $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_4H_3S)(CO)_6\{P(C_4H_3S)Ph_2\}]$

The reaction of $Ph_2(C_4H_3S)PSe$ with $[Ru_3(CO)_{12}]$ affords the open triangular 50-electron cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P(C_4H_3S)Ph_2\}_2]$ (**1**) and the 48-electron cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}PPh_2)(\mu\text{-}C_4H_3S)(CO)_6\{P(C_4H_3S)Ph_2\}]$ (**2**) derived by the multiple fragmentation of one phosphine ligand on the metal triangle. The same cluster core is also exhibited by a major ionic fragment detected in the mass spectrum of **1**, suggesting that **2** is a secondary product derived from decomposition of **1**.

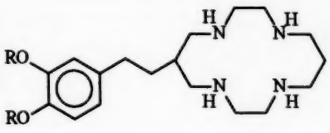


A. McAuley, S. Subramanian

Inorg. Chim. Acta 300–302 (2000) 477

Synthesis and characterization of Ni(II) and Cu(II) complexes of 6-(β-(3,4-dimethoxyphenylethyl))-cyclam, (L_1) and 6-(β-(3,4-dihydroxyphenylethyl))-cyclam, (H_2L_2) (cyclam = 1,4,8,11- tetraazacyclotetradecane). X-ray crystal structures of $[Cu(L_1)Br_2]$ and $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$ and metal ion templated formation of multinuclear macrocyclic complexes

The Ni(II) and Cu(II) complexes of the catechol appended cyclam ligand, H_2L_2 and its precursor, L_1 have been prepared and characterized. The complexes $[Cu(L_1)Br_2]$ and $[Cu(H_2(BrL_2))Br]Br\cdot H_2O$ have been characterized by single-crystal X-ray crystallography and formation of multinuclear cations on a Fe(III) ion template by the complexes of H_2L_2 have been explored by UV–Vis and EPR spectroscopy.

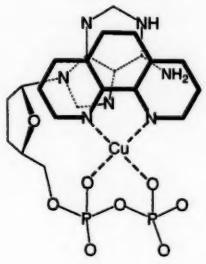


Emanuela M. Bianchi, S. Ali A. Sajadi, Bin Song, Helmut Sigel

Inorg. Chim. Acta 300–302 (2000) 487

Intramolecular stacking interactions in mixed ligand complexes formed by copper(II), 2,2′-bipyridine or 1,10-phenanthroline, and monoprotonated or deprotonated adenosine 5′-diphosphate (ADP^{3-}). Evaluation of isomeric equilibria

The stacked isomer of $Cu(Phen)(ADP)^-$ occurs in aqueous solution with a formation degree of about 85%; the one of the monoprotonated complex, Cu(Phen)(H;ADP), where the proton is at the terminal β-phosphate group, is of similar order as are those of the corresponding complexes formed with adenosine 5′-mono- and 5′-triphosphate.

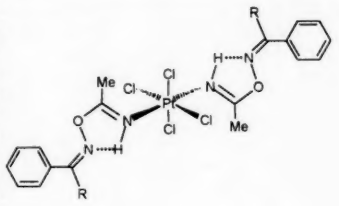


Dmitrii A. Garnovskii, M. Fátima C. Guedes da Silva, Tatyana B. Pakhomova, Gabriele Wagner, M. Teresa Duarte, João J.R. Fraústo da Silva, Armando J.L. Pombeiro, Vadim Yu. Kukushkin

Inorg. Chim. Acta 300–302 (2000) 499

Iminoacylation. Part 6: Coupling of chloro- and amidoximes Ar(R)C=NOH (R = Cl, NH_2) with acetonitrile ligands coordinated to platinum(IV)

Acetonitrile ligands in the Pt(IV) center *trans*-$[PtCl_4(MeCN)_2]$ are activated towards nucleophilic attack behaving as iminoacylating agents of oximes, $RR^1C{=}NOH$. Addition of chloro- and amidoximes to the acetonitrile ligands leads to the complexes with iminoacylated species *trans*-$[PtCl_4\{NH{=}C(Me)\text{-}ON{=}CRR^1\}_2]$. X-ray crystal structure determination of two iminoacylated compounds (R/R^1 = Cl/C_6H_4-*p*-Me, Cl/C_6H_4-*p*-NO_2) are presented.

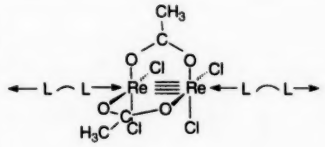


Yan Ding, Sophia S. Lau, Phillip E. Fanwick, Richard A. Walton

Inorg. Chim. Acta 300–302 (2000) 505

Polymeric dirhenium(III) complexes of the type $[cis\text{-}Re_2(O_2CCH_3)_2Cl_4(LL)]_n$ involving the symmetrical linker ligands pyrazine, 4,4′-bipyridine, and methylenebis(diphenylphosphine oxide)

The dirhenium(III) synthon *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(H_2O)_2$ reacts with the ligands pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy) and methylenebis(diphenylphosphine oxide) ($dppmO_2$) to form polymeric complexes of the type $[cis\text{-}Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(\mu\text{-}LL)]_n$ (LL = pyz (**1**), 4,4′-bpy (**3**) or $dppmO_2$ (**4**)). Crystals of the tetrarhenium complex $[cis\text{-}Re_2(\mu\text{-}O_2CCH_3)_2Cl_4(pyz)]_2(\mu\text{-}pyz)$ (**2**), have also been obtained, and all four compounds **1**–**4** have been characterized by X-ray crystallography.

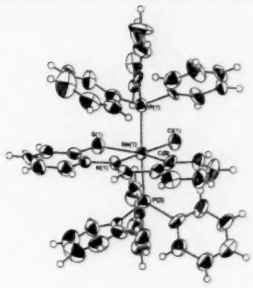


Tatsuya Kawamoto

Inorg. Chim. Acta 300–302 (2000) 512

Activation of C–H and C–Cl bonds in the reactions of 2-substituted benzothiazolines with $[RhCl(PPh_3)_3]$

The reactions of 2-phenylbenzothiazoline or 2-(2,6-dichlorophenyl)benzothiazoline with $[RhCl(PPh_3)_3]$ afforded the neutral rhodium(III) complexes $[RhCl(S–N–C)(PPh_3)_2]$ $(S–N–C = C_6H_4SN=CHC_6H_4^{2-})$ and $[RhCl(S–N–C(Cl))(PPh_3)_2]$ $(S–N–C(Cl) = C_6H_4SN=CHC_6H_3Cl^{2-})$ through the activation of C–H and C–Cl bonds, respectively. To evaluate whether C–Cl activation is more favourable than C–H activation, 2-(2-chlorophenyl)benzothiazoline was reacted with $[RhCl(PPh_3)_3]$. The reaction shows that C–Cl bond activation is preferred in this system.

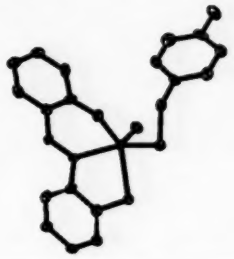


Frank J. Femia, Xiaoyuan Chen, John W. Babich, Jon Zubieta

Inorg. Chim. Acta 300–302 (2000) 517

Oxorhenium(V) complexes containing tridentate Schiff-base and monothiol coligands

The reaction of $[n\text{-}(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ with $[HOC_6H_4C(H)NC_6H_4SH]$ yields $[ReOBr\{\eta^3\text{-}(OC_6H_4C(H)NC_6H_4S)\}]$. The reactions of $[n\text{-}(C_4H_9)_4N][ReOBr_4(OPPh_3)]$ with $[HOC_6H_4C(H)NC_6H_4SH]$ and the appropriate thiolate ligands yield the complexes $[ReO\{\eta^3\text{-}(OC_6H_4C(H)NC_6H_4S)\}(\eta^1\text{-}C_6H_4X\text{-}4\text{-}S)]$ (X = H, Br, Cl, F, and OCH_3), and a cationic oxorhenium(V) species, $[ReO\{\eta^3\text{-}(OC_6H_4C(H)NC_6H_4S)\}(\eta^1\text{-}C_5H_4NH\text{-}2\text{-}S)][Br]$.

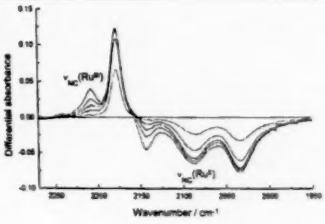


Joseph P. al Dulaimi, Robin J.H. Clark, Marcia Saavedra S., Md. Abdus Salam

Inorg. Chim. Acta 300–302 (2000) 525

Redox properties of two new ruthenium(III) isocyanide complexes, *trans*-$[NBu_4][RuX_4(CNTM)_2]$ (X = Cl or Br, CNTM = *p*-tolylsulfonylmethylisocyanide)

In situ IR and UV–Vis spectroelectrochemical studies have shown that the reduction of *trans*-$[RuX_4(CNTM)_2]^-$ (X = Cl or Br, CNTM = *p*-tolylsulfonylmethylisocyanide) in acetonitrile and subsequent oxidation yields *mer,trans*-$[RuX_3(CNTM)_2(NCMe)]$. Oxidation of *trans*-$[RuX_4(CNTM)_2]^-$ and subsequent reduction yields the same product.

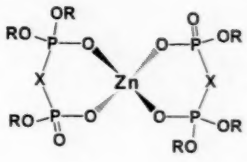


A. Müller-Hartmann, H. Vahrenkamp

Inorg. Chim. Acta 300–302 (2000) 531

Binary zinc-oligophosphate complexes

Diorganodiphosphates (DPP^{2-}), triorganodiphosphates (TPP^-), a diorganotriphosphate $(DPPP^{3-})$, and a triorganomethylenediphosphonate $(TPCP^-)$ were reacted with zinc perchlorate to form the corresponding binary complexes. Of these Zn(DPP) and $Zn_3(DPPP)_2$ were assigned as coordination polymers, while $Zn(TPP)_2$ and $Zn(TPCP)_2$ are molecular complexes.

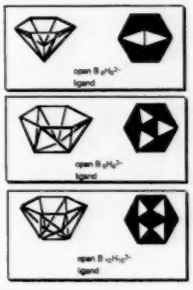


R.B. King

Inorg. Chim. Acta 300–302 (2000) 537

Face-localized bonding models for borane cage ligands in transition metal coordination chemistry

The change in electron count from $2n + 2$ skeletal electrons for metal-free borane *closo* deltahedra having the maximum number of degree 4 and 5 vertices to $2n$ skeletal electrons for metallaborane *isocloso* deltahedra with the metal at a single degree 6 vertex can be rationalized by a major change in the skeletal bonding topology from globally delocalized in the *closo* deltahedra to face-localized in the *isocloso* deltahedra.

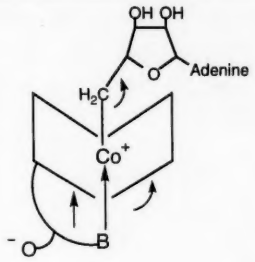


Jeanne M. Sirovatka, Anthony K. Rappé, Richard G. Finke

Inorg. Chim. Acta 300–302 (2000) 545

Molecular mechanics studies of coenzyme B_{12} complexes with constrained Co–N(axial-base) bond lengths: introduction of the universal force field (UFF) to coenzyme B_{12} chemistry and its use to probe the plausibility of an axial-base-induced, ground-state corrin butterfly conformational steric effect

The universal force field (UFF) is used to (i) test the applicability of UFF to model a range of known cobalamin structures including adenosylcobalamin (AdoCbl), and (ii) to probe the steric-only, ground-state corrin butterfly conformational theory (shown in the inset), a leading hypothesis for how AdoCbl-binding enzymes accelerate Co–C cleavage by $\sim 10^{12}$ in the AdoCbl-enzyme·substrate complex.

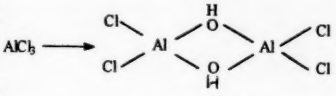


Zbyněk Černý, Jiří Macháček, Jiří Fusek, Bohuslav Čásenský, Otomar Kříž, Dennis G. Tuck

Inorg. Chim. Acta 300–302 (2000) 556

^{27}Al NMR studies of the hydrolysis of aluminium(III) chloride in non-aqueous media

The treatment of solid $AlCl_3$ with benzene gives a solution containing a number of derivative species, which have been characterised by ^{27}Al NMR spectroscopy. The solutes include $H[AlCl_4]$ and $H[AlCl_3(OH)]$, higher aggregates of these, and a non-ionic species $[Cl_2Al(OH)]_2$; the formation of this last explains the reported identification of related structures in preparative work involving benzene and nominally anhydrous $AlCl_3$.

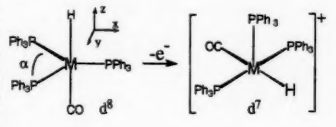


Alan M. Bond, David G. Humphrey, Dmitri Menglet, Georgii G. Lazarev, Ron S. Dickson, Truc Vu

Inorg. Chim. Acta 300–302 (2000) 565

Structural assignment of the stable carbonylhydridotris(triphenylphosphine)iridium(II) cation and spectroscopic and voltammetric identification of the transient Ir(III) dication and its decomposition pathway

$[Ir^{II}H(CO)(PPh_3)_3]^+$ and $[Ir^{III}H(CO)(PPh_3)_3]^{2+}$ have been characterised spectroscopically after their generation by electrochemical oxidation of $IrH(CO)(PPh_3)_3$ in dichloromethane. EPR and density functional calculations are consistent with the initial one-electron oxidation leading to a structural change from trigonal bipyramidal to square pyramidal.

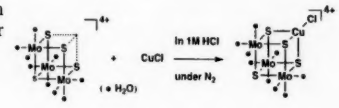


Haruo Akashi, Takashi Shibahara

Inorg. Chim. Acta 300–302 (2000) 572

Molybdenum–copper–sulfur Mo_3CuS_4 cubes

Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with CuCl in 1 M HCl gives a novel cubane-type cluster $[Mo_3CuS_4Cl(H_2O)_9]^{4+}$.

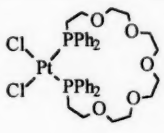


Gary M. Gray, Dale C. Smith Jr., Christina H. Duffey

Inorg. Chim. Acta 300–302 (2000) 581

$^{31}P\{^1H\}$ NMR spectroscopic and X-ray crystallographic studies of conformational dynamics in *cis*-M{$Ph_2P(CH_2CH_2O)_5CH_2$-CH_2PPh_2-P,P′} (M = $Mo(CO)_4$, $PtCl_2$) metallacrown ethers

Exchange between symmetrical and unsymmetrical conformers of *cis*-M{$Ph_2P(CH_2$-$CH_2O)_5CH_2CH_2PPh_2$-P,P′} (M = $Mo(CO)_4$ and $PtCl_2$) metallacrown ethers has been studied using variable temperature $^{31}P\{^1H\}$ NMR spectroscopy. X-ray crystallographic studies suggest that the symmetrical conformers are favored by bulky metal centers.

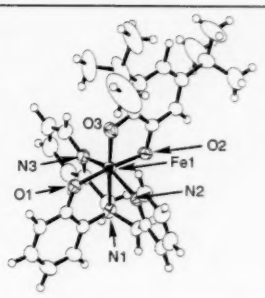


Ryo Yamahara, Seiji Ogo, Yoshihito Watanabe, Takuzo Funabiki, Koichiro Jitsukawa, Hideki Masuda, Hisahiko Einaga

Inorg. Chim. Acta 300–302 (2000) 587

(Catecholato)iron(III) complexes with tetradentate tripodal ligands containing substituted phenol and pyridine units as structural and functional model complexes for the catechol-bound intermediate of intradiol-cleaving catechol dioxygenases

Structural model complexes for the catechol-bound intermediate of protocatechuate 3,4-dioxygenase (3,4-PCD): $[Fe^{III}(L_{R',R''})(DBC)]$ ($L_{R',R''}$ = {2-hydroxy-3-R′-5-R″-phenyl-bis-(2-pyridylmethyl)amine}); **1a**: R′,R″ = H,H; **1b**: R′,R″ = Me,Me; and **1c**: R′,R″ = H,Cl, DBC = 3,5-di-*tert*-butylcatecholato) have been synthesized. Oxygenation of the bound DBC on **1** in the presence of O_2 is discussed based on the Lewis basicity of the tripodal ligand containing the substituted phenolato group which is introduced to mimic the Tyr408 ligand of 3,4-PCD.

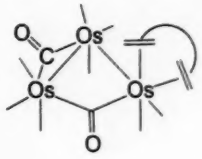


Maarten J. Bakker, Frank W. Vergeer, František Hartl, Omar S. Jina, Xue-Zhong Sun, Michael W. George

Inorg. Chim. Acta 300–302 (2000) 597

Mechanistic study of the photofragmentation of the clusters $[Os_3(CO)_{10}(diene)]$ (diene = *cis*-1,3-butadiene, 1,3-cyclohexadiene): direct observation of the open-triangle primary photoproduct with nanosecond time-resolved infrared and UV–Vis spectroscopy

The photofragmentation pathway of clusters of the type $[Os_3(CO)_{10}(1,3\text{-diene})]$ into $[Os(CO)_3(1,3\text{-diene})]$ upon near-UV irradiation was thoroughly investigated. For the primary photoproduct with a lifetime of approximately 100 ns, observed with nanosecond time-resolved UV–Vis and IR spectroscopy, a coordinatively unsaturated open-triangle structure with two bridging carbonyl groups is proposed.

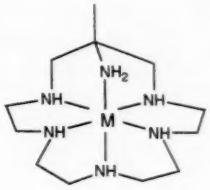


Paul V. Bernhardt, Geoffrey A. Lawrance, Mery Napitupulu, Gang Wei

Inorg. Chim. Acta 300–302 (2000) 604

Synthesis and complexes of the sexidentate macrocycle 15-methyl-1,4,7,10,13-pentaazacyclohexadecan-15-amine

Metal-directed synthesis leads to the potentially sexidentate pendant arm macrocyclic ligand 15-methyl-1,4,7,10,13-pentaazacyclohexadecan-15-amine (**1**) which forms octahedral complexes with Co(III), Cr(III) and Fe(III), binding with two non-equivalent N_3 facial units as determined from the X-ray structure of the cobalt(III) complex.

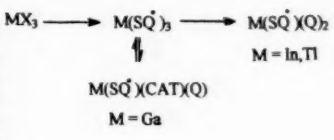


Martyn A. Brown, Ahmed A. El-Hadad, Bruce R. McGarvey, Raymond C.W. Sung, Arun K. Trikha, Dennis G. Tuck

Inorg. Chim. Acta 300–302 (2000) 613

Comparative studies of electron transfer in orthoquinone derivatives of gallium, indium and thallium

A series of derivatives of the elements gallium, indium and thallium and substituted orthoquinones demonstrate that interligand single electron transfer is the most important process only in the case of gallium. With complexes of the heavier elements, ligand to metal electron transfer results in the preferential formation of M(I) derivatives from unstable M(III) products. An unusual gallium complex with both semiquinone and catecholate ligands has been structurally characterised.

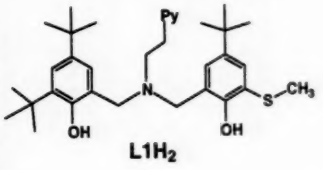


Masayasu Taki, Hideyuki Kumei, Shigenori Nagatomo, Teizo Kitagawa, Shinobu Itoh, Shunichi Fukuzumi

Inorg. Chim. Acta 300–302 (2000) 622

Active site models for galactose oxidase containing two different phenol groups

Model complexes of the active site of galactose oxidase (GAO) have been developed using a new ligand carrying two different phenol groups (**L1H$_2$**). The structure and physicochemical properties of the diphenolate complexes $[M(II)(L1^{2-})(py)]$ (M = Cu and Zn, py = pyridine) as well as those of the corresponding phenoxyl radical/phenolate complexes of $M(II)(L1^{\bullet -})$ have been explored.

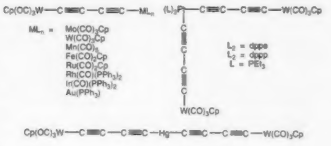


Michael I. Bruce, Ben C. Hall, Paul J. Low, Mark E. Smith, Brian W. Skelton, Allan H. White

Inorg. Chim. Acta 300–302 (2000) 633

Heterometallic complexes containing C_4 chains. X-ray structures of $\{Cp(OC)_3W\}C{\equiv}CC{\equiv}C\{Ir(CO)(PPh_3)_2(O_2)\}$ and *cis*-$Pt\{C{\equiv}CC{\equiv}C[W(CO)_3Cp]\}_2(PEt_3)_2$

Heterometallic diyndiyl complexes containing tungsten linked to metals of Groups 6–12 through a C_4 bridge are prepared by simple derivatisation of $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$. Rhodium and iridium complexes react with dioxygen at the Group 9 metal centre. X-ray determined structures of $\{Cp(OC)_3WCC{\equiv}C\{Ir(CO)(PPh_3)_2(O_2)\}$ and *cis*-$Pt\{C{\equiv}CC{\equiv}C\text{-}[W(CO)_3Cp]\}_2(Pet_3)_2$ are reported.

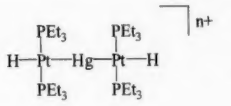


Julian A. Davies, Cassandra T. Eagle, David G. Farrar, Pannee Burckel

Inorg. Chim. Acta 300–302 (2000) 645

Electrochemical synthesis and spectroscopic characterization of a mercury–platinum–hydride complex

Controlled potential bulk reductive electrolysis of *trans*-$[PtI_2(PEt_3)_2]$ at a mercury pool electrode in 5:2 C_6H_5CN:C_6H_6 (saturated with $NaClO_4$) at an Hg pool electrode at -1.5 V (vs. Ag/AgCl) and at ca. 0°C proceeded by an overall one-electron process. $^{31}P\{^1H\}$ NMR spectroscopy revealed only two phosphorus-containing species, *trans*-$[PtI_2(PEt_3)_2]$ and a novel diplatinum complex. Additional analyses by ^1H and $^{195}Pt\{^1H\}$ NMR spectroscopy, SEM-EDS, and ICP-AES methods revealed formation of a mercury–diplatinum–hydride complex via mercury abstraction from the electrode and hydrogen abstraction from the solvent.

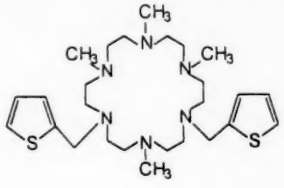


Carla Bazzicalupi, Andrea Bencini, Antonio Bianchi, Valentina Fedi, Claudia Giorgi, Piero Paoletti, Lorenzo Tei, Barbara Valtancoli

Inorg. Chim. Acta 300–302 (2000) 653

Coordination properties of a new hexaazamacrocycle containing thiophene units as pendant arms

The hexaaza macrocycle **L2** is able to selectively coordinate Cd(II) and Pb(II) over Zn(II) in aqueous solution. The metal complexes are readily extractable in organic solvents from aqueous solutions at neutral pH, due to the hydrophobic character of the thiophene side arms. Such characteristics make this ligand a promising selective extracting agent for metal cations from aqueous solutions.



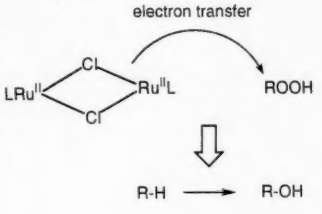
L2

Takahiko Kojima, Hidenobu Matsuo, Yoshihisa Matsuda

Inorg. Chim. Acta 300–302 (2000) 661

Catalytic hydrocarbon oxygenation by ruthenium–pyridylamine complexes with alkyl hydroperoxides: a mechanistic insight

Bis-μ-chloro dinuclear Ru(II) complexes, $[RuCl(L)]_2[ClO_4]_2$ (L = tris(2-pyridylmethyl)-amine (TPA) and tris(5-methyl-2-pyridylmethyl)amine (5-Me_3–TPA)) showed catalytic hydrocarbon oxygenation by using alkyl hydroperoxides via Haber–Weiss-type reactions. Reactivity of the complexes were governed first by their redox potentials and second by the environment around the ruthenium centers.

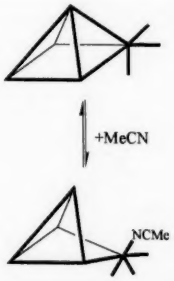


David H. Farrar, Anthony J. Poë, Ying Zheng

Inorg. Chim. Acta 300–302 (2000) 668

Kinetic and thermodynamic studies of reversible adduct formation between $Ru_5C(CO)_{15}$ and acetonitrile

Kinetic and equilibrium studies have been made of the reversible addition of acetonitrile to the carbido cluster $Ru_5C(CO)_{15}$, shown schematically here only by the Ru framework and relevant ligands on one Ru atom. The transition state for addition is very early and the favourable thermodynamic parameters for addition indicate a considerable relief of steric strain in the cluster.

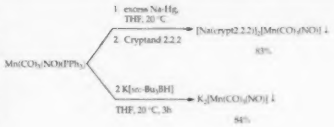


Yu-Sen Chen, John E. Ellis

Inorg. Chim. Acta 300–302 (2000) 675

Highly reduced organometallics 52. Synthesis and chemistry of tricarbonylnitrosylmanganate(2 −), $[Mn(CO)_3(NO)]^{2-}$

Reduction of tricarbonylnitrosyltriphenylphosphinemanganese by either sodium amalgam or potassium tri-*sec*-butylborohydride affords high yields of the first example of a mixed mononuclear carbonylnitrosylmetallate dianion, tricarbonylnitrosylmanganate(2 −). The latter was isolated as thermally robust, but quite air sensitive, sodium(cryptand 2.2.2) and potassium salts. These substances are isoelectronic with the long known corresponding tetracarbonylferrate(2 −) salts and undergo entirely analogous reactions with chlorotriphenylstannane, tetracarbonylnitrosylmanganese and pentacarbonyliron to provide new bimetallic species.

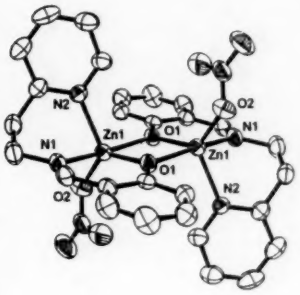


S.S. Tandon, S. Chander, L.K. Thompson

Inorg. Chim. Acta 300–302 (2000) 683

Ligating properties of tridentate Schiff base ligands, 2-[[(2-pyridinylmethyl)imino]methyl] phenol (HSALIMP) and 2-[[[2-(2-pyridinyl)ethyl]imino]methyl]-phenol (HSALIEP) with zinc(II), cadmium(II), nickel(II) and manganese(III) ions. X-ray crystal structures of the $[Zn(SALIEP)(NO_3)]_2$ dimer, $[Mn(SALIEP)_2](ClO_4)$, and $[Zn(AMP)_2(NO_3)_2]$

A series of zinc(II), cadmium(II), nickel(II), and maganese(III) complexes with two potentially tridentate (NNO) Schiff base ligands - 2 - [[2 - pyridinylmethyl)imino]methyl]-phenol(HSALIMP) and 2-[[2-pyridinyl)-ethyl]imino]methyl]phenol (HSALIEP) have been synthesized and structurally characterized through IR, ^1H, ^{13}C, and 2D NMR spectroscopy and in two cases by X-ray crystallography. HSALIMP behaves as a tridentate (NNO) or a bidentate (NN) ligand, depending upon the nature of the anion. However HSALIEP, a similar ligand with one additional carbon in the chain, acts as a tridentate ligand (NNO), with the phenolate oxygen deprotonated, irrespective of the nature of the anion, forming dimeric compounds of 1:1 metal:ligand stoichiometry with zinc(II) (**IV**, **V**, **VI**) and cadmium(II) (**VII**) ions.

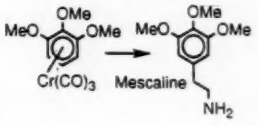


Françoise Rose-Munch, René Chavignon, Jean-Philippe Tranchier, Vanessa Gagliardini, Eric Rose

Inorg. Chim. Acta 300–302 (2000) 693

Mescaline synthesis via tricarbonyl (η^6-1,2,3-trimethoxybenzene)chromium complex

Treatment of tricarbonyl(η^6-1,2,3-trimethoxybenzene)chromium complex with acetonitrile carbanion and then with iodine followed by reduction of the nitrile function gives mescaline.

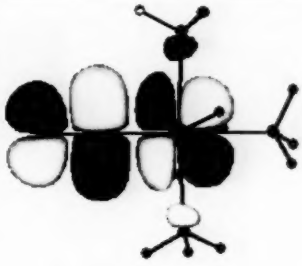


Sergey I. Gorelsky, Sebastião C. da Silva, A.B.P. Lever, Douglas W. Franco

Inorg. Chim. Acta 300–302 (2000) 698

Electronic spectra of *trans*-$[Ru(NH_3)_4(L)NO]^{3+/2+}$ complexes

Density functional theory (DFT) with local, non-local and hybrid functionals has been used to obtain the geometry of a series of nitrosyl–metal complexes $[Ru(NH_3)_4(L)NO]^{n+}$, where $L = NH_3$, H_2O, pyrazine and pyridine ($n = 3$), Cl^- and OH^- ($n = 2$). The electronic structures and the assignment of the bands in the electronic spectra of these complexes are discussed.

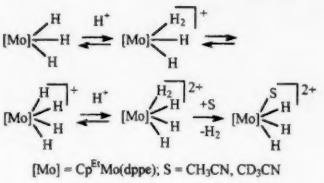


Dolores Morales, Rinaldo Poli, Jacques Andrieu

Inorg. Chim. Acta 300–302 (2000) 709

Protonation and oxidation chemistry of a pentaethylcyclopentadienyl-containing molybdenum(IV) trihydride complex

The protonation and oxidation studies of $(C_5Et_5)MoH_3(dppe)$ and $(C_5Et_5)MoD_3(dppe)$ in MeCN show important differences with respect to previously reported studies on the (C_5Me_5) analogs. The differences may be attributed to a kinetic stabilization of the products, which is steric in nature. This study includes the spectroscopic identification of a new product from a double protonation process, namely $[(C_5Et_5)MoH_3(dppe)(MeCN)]^{2+}$.

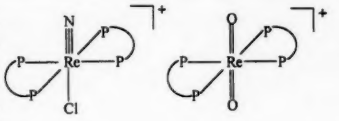


Vivian Wing-Wah Yam, Yung-Lin Pui, Keith Man-Chung Wong, Kung-Kai Cheung

Inorg. Chim. Acta 300–302 (2000) 721

Synthesis, structural characterisation, photophysics, photochemistry and electrochemistry of nitrido- and *trans*-dioxorhenium(V) complexes with substituted dppe ligands (dppe = bis-(diphenylphosphino)ethane)

A series of nitrido- and *trans*-dioxorhenium(V) complexes with substituted dppe ligands have been synthesized and characterized, and their photophysics and electrochemistry studied. The excited state chemistry of $[Re(N)(dmppe)_2(MeCN)]^{2+}$ has also been investigated. The structures of $[Re(N)(dmppe)_2Cl]^{+}$ and $[Re(O)_2(dmppe)_2]^{+}$ have been determined by X-ray crystallography.

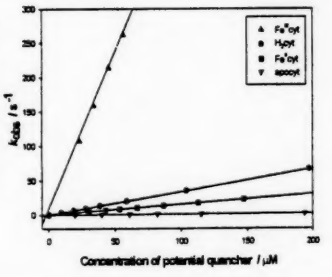


Scott M. Tremain, Nenad M. Kostić

Inorg. Chim. Acta 300–302 (2000) 733

Fate of the excited triplet state of zinc cytochrome *c* in the presence of iron(III), iron(II), iron-free, and heme-free forms of cytochrome *c*

We study, by laser flash photolysis, the mechanism of quenching the triplet state of zinc cytochrome *c*. Iron(III) form of cytochrome *c* strongly quenches ^{3}Zncyt by electron transfer. Iron(II) and iron-free forms of cytochrome *c* weakly quench ^{3}Zncyt by energy transfer. Heme-free form of cytochrome *c* does not quench ^{3}Zncyt. Trace contamination by redox agents can spoil the experiments.

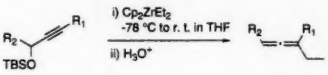


Ryuichiro Hara, Yasuyuki Ura, Shouquan Huo, Kayoko Kasai, Noriyuki Suzuki, Tamotsu Takahashi

Inorg. Chim. Acta 300–302 (2000) 741

Allene formation by coupling of propargylic ethers with olefins via β-alkoxide elimination of zirconacycle intermediates

Propargylic ethers reacted with diethylzirconocene to give allene derivatives via β-alkoxide elimination after hydrolysis.

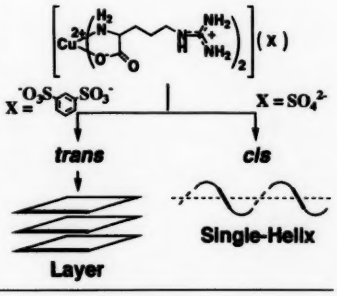


Nayumi Ohata, Hideki Masuda, Osamu Yamauchi

Inorg. Chim. Acta 300–302 (2000) 749

Dianion-controlled supramolecular assembly of copper(II)-arginine complex ion

The supramolecular assemblies of $[Cu(L\text{-}arg_2)]^{2+}$–$X^{2-}$ systems, where arg and X^{2-} refer to arginine and SO_4^{2-} or 1,3-benzenedisulfonate (m-bs^{2-}), respectively, have been revealed to have a right-handed double-strand single-helical structure when $X^{2-} = SO_4^{2-}$ and a layer structure when $X^{2-} = m\text{-}bs^{2-}$. They depend on the *cis–trans* geometry of the Cu(II) plane, which is predictable from the structural requirements for the hydrogen bonding with X^{2-}.

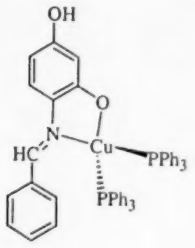


Torsten Sixt, Wolfgang Kaim

Inorg. Chim. Acta 300–302 (2000) 762

Copper(I) complexes with N,O-donor Schiff base ligands related to intermediate forms of the TPQ cofactor in amine oxidases

Neutral complexes $(PPh_3)_2Cu(L)$ were obtained from $(PPh_3)_2Cu(NO_3)$ and the deprotonated forms of the ligands 2-(benzylideneimino)phenol (BimOH), 4-(benzylideneimino)-resorcinol ($Bim(OH)_2$) and *N*-(2,4-dihydroxy-5-isopropylphenyl)acetamide ($DipaH_3$) which are related to Schiff base intermediates of the topaquinone (TPQ) cofactor in the enzymatic cycle of copper-dependent amine oxidases. Compound $(Bim(OH)O)Cu(PPh_3)_2 \cdot 0.5CH_3OH$ was structurally analyzed to reveal intermolecular hydrogen bonds involving the phenolic hydroxyl substituent, the coordinated phenolate oxygen atom and the methanol solvate molecule.

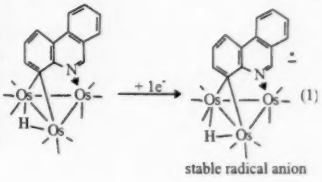


Edward Rosenberg, Md. J. Abedin, Dalia Rokhsana, Domenico Osella, Luciano Milone, Carlo Nervi, Jan Fiedler

Inorg. Chim. Acta 300–302 (2000) 769

The electrochemical behaviour of electron deficient benzoheterocycle triosmium clusters

Although a series of electron deficient triosmium cluster benzoheterocycle complexes are all structurally very similar in terms of their interaction with the metal core their electrochemical behaviour varies widely with some forming stable radical anions and others undergoing chemical reaction after electrochemical reduction.

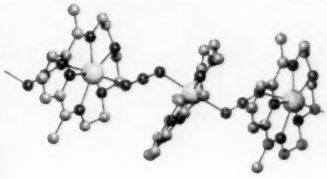


Amandeep K. Sra, Jean-Pascal Sutter, Philippe Guionneau, Daniel Chasseau, Jatinder V. Yakhmi, Olivier Kahn

Inorg. Chim. Acta 300–302 (2000) 778

Example of a single *trans*-azido-bridged Mn(II) chain: synthesis, structural and magnetic characteristics

A rare example of a single bridged $\mu_{1,3}$-azido-Mn(II) 1-D architecture of formula $\{MnLN_3(PF_6)\}_n$ is described. The compound consists of Mn(II) ions surrounded by a pentadendate ligand in equatorial coordination and linked by single end-to-end azido bridges. Magnetic susceptibility measurements indicate long range antiferromagnetic correlation between the Mn(II) centres below 30 K ($J = -4.8\ cm^{-1}$, $H = -J\Sigma\ S_iS_{i+1}$).

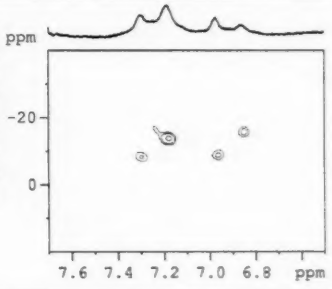


Markus Galanski, Bernhard K. Keppler

Inorg. Chim. Acta 300–302 (2000) 783

Is reduction required for antitumour activity of platinum(IV) compounds? Characterisation of a platinum(IV)–nucleotide adduct [enPt($OCOCH_3$)$_3$(5′-GMP)] by NMR spectroscopy and ESI-MS

In the present study [enPt($OCOCH_3$)$_4$] was reacted with 5′-GMP at 37°C. The time dependent attack of the nucleotide could be followed by the release of the acetato ligand detected in a very sensitive way by ^1H NMR spectroscopy. It was shown by ^{15}N,^1H-ge-HMQC NMR spectroscopy that Pt(IV)-5′-GMP species were formed. Moreover, the adduct [enPt($OCOCH_3$)$_3$(5′-GMP)] could be detected by ESI-MS.

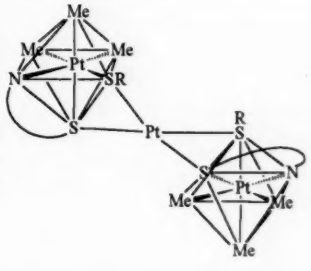


Núria Duran, William Clegg, Kelly A. Fraser, Pilar González-Duarte

Inorg. Chim. Acta 300–302 (2000) 790

The reaction chemistry of 2- and 3-aminoalkanethiols with $[PtMe_3I]_4$: a new example of the structural diversity of metal thiolates

The substitution reaction proceeds very differently depending on the nature of the aminoalkanethiolate ligand and the varied structures of the seven complexes reported provide a remarkable example of the structural diversity of metal thiolates. In the case of 2-dimethylaminoethanethiol the reaction proceeds with the concomitant partial reduction of Pt(IV) to Pt(II) as shown in the X-ray crystal structure.

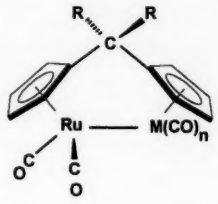


Thomas E. Bitterwolf, Abdul A. Saygh, Joyce E. Shade, Arnold L. Rheingold, Glenn P.A. Yap, Louise M. Lable-Sands

Inorg. Chim Acta 300–302 (2000) 800

Synthesis and photochemistry of ring-coupled heterobimetallic compounds of ruthenium. The molecular structures of $RuM(CO)_5(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4CR_2C_5H_4)$, where M = Mo, R = CH_3; M = W, R = H, $[Ru(CO)_2][Mo(CO)_3Cl](\mu\text{-}\eta^5,\eta^1\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_3)$ and $[W(CO)_3][Ru(CO)_2Cl](\mu\text{-}\eta^5,\eta^1\text{:}\eta^5\text{-}C_5H_4CH_2C_5H_3)$

Reaction of $Ru(CO)_2(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_4CR_2C_5H_4)$, where R = H or CH_3, with metal carbonyl reagent yields heterobimetallic compounds of the form $RuM(CO)_5[\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4C(CH_3)_2C_5H_4]$, M = Mo or W ($n = 5$), Fe ($n = 4$), and Ni ($n = 3$). Triphenylphosphine substitution occurs upon photolysis with formation of both isomeric products in the case of the Ru/Mo compound, but only a single isomer for the Ru/Fe compound. In the absence of potential ligands, photolysis results in formation of twist isomers arising from insertion of a metal into a ring C–H bond.

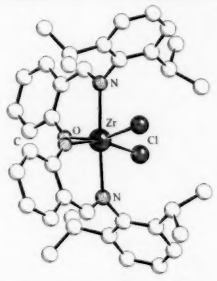


Joachim Strauch, Timothy H. Warren, Gerhard Erker, Roland Fröhlich, Pauli Saarenketo

Inorg. Chim. Acta 300–302 (2000) 810

Formation and structural properties of salicylaldiminato complexes of zirconium and titanium

Salicylaldimines (lig-H) react with $(Me_2N)_2MX_2$ (M = Ti, Zr; X = NMe_2 or Cl) to yield the octahedral $(lig)_2MX_2$ complexes that exhibit specific *trans*-oxygen (X = NMe_2) or *trans*-nitrogen (X = Cl) coordination in most cases. The $(lig)_2MCl_2$ systems were activated with methylalumoxane to give ethene polymerisation catalysts.



Robin C. Lasey, Sunandita S. Banerji, Michael Y. Ogawa

Inorg. Chim. Acta 300–302 (2000) 822

Synthesis and characterization of a sequence-specific DNA-binding protein that contains ruthenium polypyridyl centers

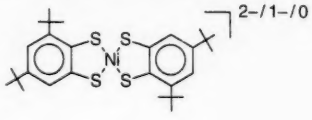
A chimeric metallo–DNA-binding protein, (GBR-CC)Ru, was prepared that contains the native DNA-binding domain of the GCN-4 transcription factor (GBR), a synthetic α-helical coiled-coil dimerization site (CC) and a ruthenium polypyridyl complex (Ru) attached to a surface-exposed cysteine residue.

Dieter Sellmann, Herbert Binder, Daniel Häußinger, Frank W. Heinemann, Jörg Sutter

Inorg. Chim. Acta 300–302 (2000) 829

Transition metal complexes with sulfur ligands Part CXLIV. Square planar nickel complexes with NiS_4 cores in three different oxidation states: synthesis, X-ray structural and spectroscopic studies

The nickel thiolate complexes $[Ni(^{tbu}S_2')_2]^{n-}$ with $n = 2, 1, 0$ have been synthesized and have formally Ni^{II}, Ni^{III} and Ni^{IV} centers. X-ray structure analyses, spectroscopic investigations (UV–Vis, NMR, EPR and XPS), and reactions with H^+ and CO indicate that the features of $[Ni(^{tbu}S_2')_2]$ complexes are due to the $[NiS_4]$ core and not to an electron delocalization beyond the $[NiS_4]$ core into the benzene rings.

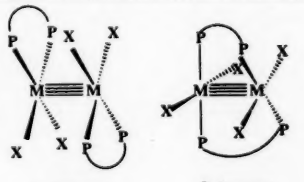


Sophie Blasco, Isabelle Demachy, Yves Jean, Agustí Lledós

Inorg. Chim. Acta 300–302 (2000) 837

Structural preferences of quadruply bonded bimetallic complexes. A DFT study of the chelated (α) and bridged (β) isomers in $Mo_2Cl_4(H_2P(CH_2)_nPH_2)_2$ ($n = 1, 2$)

Compounds of $M_2X_4(P\text{–}P)_2$ type (M = Mo, W; X = halide; P–P = diphosphine) may exist in two isomeric forms; chelated (α) and bridged (β). The geometries, the relative stabilities and the nature of the electronic ground state of the two isomers in $Mo_2Cl_4(H_2P(CH_2)_nPH_2)_2$ ($n = 1,2$) are studied by means of DFT calculations.

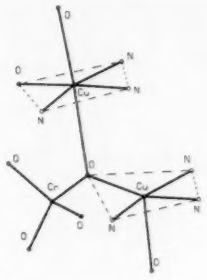


María Luisa Calatayud, Isabel Castro, Jorunn Sletten, Francesc Lloret, Miguel Julve

Inorg. Chim. Acta 300–302 (2000) 846

Syntheses, crystal structures and magnetic properties of chromato-, sulfato-, and oxalato-bridged dinuclear copper(II) complexes

Dinuclear copper(II) complexes with chromate (**1**), sulfate (**2**) and oxalate (**3** and **4**) as bridging ligands have been synthesized, structurally characterized by X-ray crystallography, and their magnetic behaviour has been investigated as a function of the temperature. The magnetic study reveals the occurrence of weak intramolecular antiferro- (**1** and **2**) and ferromagnetic (**3** and **4**) interactions.

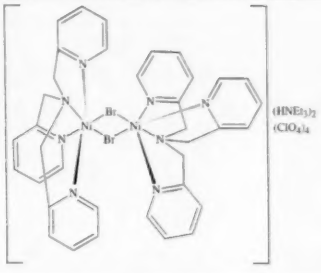


Bing Tong, Shih-Chi Chang, Everett E. Carpenter, Charles J. O'Connor, Jackson O. Lay Jr., Richard E. Norman

Inorg. Chim. Acta 300–302 (2000) 855

Di-μ-halo-bis{[tris(2-pyridylmethyl)amine-κ^4N] nickel(II)} bis(triethylammonium) tetraperchlorate: Magnetostructural studies

A crystal structure containing the $[\{NiBr\}_2]^{2+}$ unit and magnetic susceptibility studies of this complex and the Cl analog are reported. The Br dimer is more strongly ferromagnetically coupled than the Cl dimer.

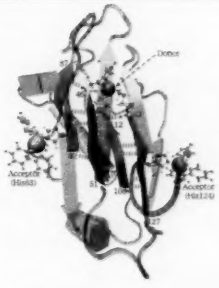


Tsutomu Kawatsu, Toshiaki Kakitani, Takahisa Yamato

Inorg. Chim. Acta 300–302 (2000) 862

A novel method for determining the electron tunneling pathway in protein

We have developed a novel method for determining the electron tunneling pathway by connecting important interatomic tunneling currents. Applying this method to Ru-modified azurins, we found that the through-bond is most frequently used, the through-space is sometimes used and the hydrogen-bond is rarely used, and that the tunneling pathway as a whole is almost straight even when it traverses some β-strands.

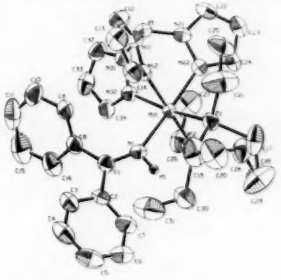


Miguel Angel Jiménez-Tenorio, Manuel Jiménez-Tenorio, M. Carmen Puerta, Pedro Valerga

Inorg. Chim. Acta 300–302 (2000) 869

Synthesis and properties of hydrotris(pyrazolyl)borate (Tp) ruthenium complexes with benzophenone imine: X-ray crystal structure of $[TpRu(HN{=}CPh_2)(PEt_3)_2][BPh_4]$

Several cationic and neutral hydrotris(pyrazolyl)borate ruthenium phosphine complexes containing benzophenone imine have been prepared and characterized; deprotonation of the imine adducts led to species containing a metalated phenyl ring instead of the expected azavinylidene derivatives.

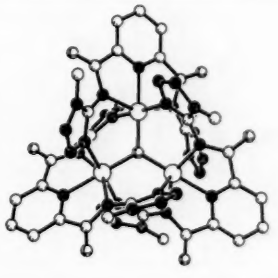


V. Coropceanu, V. Schünemann, C. Ober, M. Gerdan, A.X. Trautwein, J. Köhler, R.W. Saalfrank

Inorg. Chim. Acta 300–302 (2000) 875

A neutral triple-helical trinuclear oxo-centered mixed-valent iron complex: Mössbauer spectroscopic and magnetic susceptibility studies

The electronic properties of the trimeric oxo-centred $[Fe_3OL_3]$ complex (L is a doubly negatively charged pentadentate ligand, providing five nitrogens for iron coordination) have been investigated by Mössbauer spectroscopy and magnetic susceptibility. In order to explain the seemingly contradictory situation that the Mössbauer spectra of $[Fe_3OL_3]$ exhibit partial valence delocalisation while it is possible to analyse the magnetic data with valence-trapped ground state and exited states a theoretical treatment is presented, which includes antiferromagnetic exchange, double exchange and vibronic interactions.

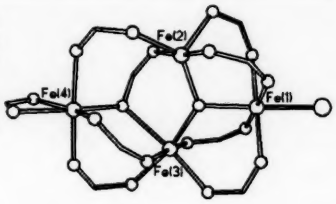


Daniela Belli Dell'Amico, Daniele Boschi, Fausto Calderazzo, Sandra Ianelli, Luca Labella, Fabio Marchetti, Giancarlo Pelizzi, Elsje Guy Frieda Quadrelli

Inorg. Chim. Acta 300–302 (2000) 882

N,N-Dialkylcarbamato μ-oxo derivatives of iron(III)

A series of *N,N*-dialkylcarbamates of iron(III), $Fe(O_2CNR_2)_3$ (R = Et, ^{i}Pr, cy, Bz) have been prepared. The μ-oxo complexes $[Fe_2O(O_2CNR_2)_4]_n$, (R = Et, cy, ^{i}Pr) are reported and $Fe_4(\mu_3\text{-}O)(O_2CN^sBu_2)_9Cl$ and $Fe_{10}(\mu_3\text{-}O)_3(\mu_4\text{-}O)_3(O_2CNEt_2)_{17}Cl$ have been structurally characterized.

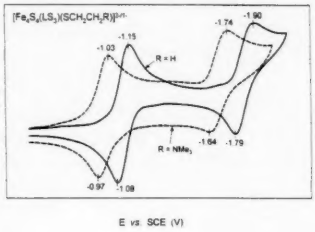


Chaoyin Zhou, James W. Raebiger, Brent M. Segal, R.H. Holm

Inorg. Chim. Acta 300–302 (2000) 892

The influence of net charge on the redox potentials of Fe_4S_4 cubane-type clusters in aprotic solvents

The redox potentials of 17 thiolate-ligated clusters have been examined in aprotic solvents, including those prepared from neutral thiolate ligands $R_3N^+\text{–}X\text{–}S^-$. It was determined that substituent inductive effects in and reduced cluster charges of [1:3] site-differentiated $[Fe_4S_4(LS_3)(SR)]^{1-}$ and $[Fe_4S_4(SR)_4]^{2+}$ (compared to the conventional $[Fe_4S_4(SR)_4]^{2-}$ clusters) can effect substantial positive potential shifts for $[Fe_4S_4]^{2+/1+}$ and $[Fe_4S_4]^{1+/0}$ redox couples. Redox potentials are relevant to the synthesis of the all-ferrous state recently demonstrated for the nitrogenase iron protein.

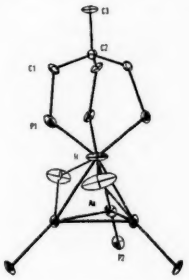


Alberto Albinati, Stanislav Chaloupka, Antonio Currao, Wim T. Klooster, Thomas F. Koetzle, Reinhard Nesper, Luigi M. Venanzi

Inorg. Chim. Acta 300–302 (2000) 903

Structural studies of the hydrido-bridged iridium gold complexes '$IrH_m\{CH_3C(CH_2PPh_2)_3\}\{Au(PR_3)\}_n$'

The X-ray structural characterization of the monogold and digold complexes $[\{CH_3C(CH_2PPh_2)_3\}HIr(\mu\text{-}H)_2\{Au(PPh_3)\}][CF_3SO_3]$ and $[\{CH_3C(CH_2PPh_2)_3\}HIr\text{-}(\mu\text{-}H)_2\{Au(P^iPr_3)\}_2][PF_6]_2$, respectively, shows that they are 'classical' hydrido-bridged species. The structural characterization, by neutron diffraction, of the trigold cluster, $[\{CH_3C(CH_2PPh_2)_3\}HIr(\mu\text{-}H)_2\{Au(PPh_3)\}]^{2+}$, confirms that only two of the three edges of the $IrAu_3$-tetrahedron are bridged by hydride ligands.

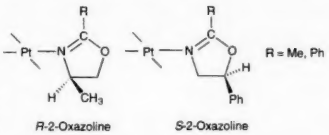


Umberto Belluco, Roberta Bertani, Fiorella Meneghetti, Rino A. Michelin, Mirto Mozzon, Giuliano Bandoli, Alessandro Dolmella

Inorg. Chim. Acta 300–302 (2000) 912

Transition metal promoted cyclization reactions of nitrile ligands: Stereochemically controlled synthesis and structural investigation of some chiral oxazoline platinum(II) complexes

The cycloaddition reactions of the nitrile ligands in *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = Me, Ph) with *S*(+)-2chloro-1-propanol or *S*(+)-2-chloro-1-phenylethanol in the presence of 2 equiv. of n-BuLi afford the corresponding chiral oxazolines having the *R* and *S* configuration, respectively, as determined by X-ray analysis. A mechanism for this stereochemically controlled conversion is proposed.

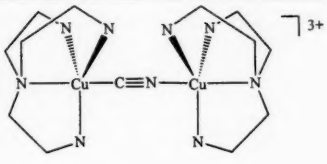


Richard J. Parker, Leone Spiccia, Boujemaa Moubaraki, Keith S. Murray, Brian W. Skelton, Allan H. White

Inorg. Chim. Acta 300–302 (2000) 922

Cyano bridged dinuclear Cu(II) complexes

Cyano bridged dinuclear copper(II) complexes of two tripodal tetradentate ligands, featuring trigonal bipyramidal copper(II) geometries with the bridging group in an axial position, exhibit medium strength antiferromagnetic coupling.



W. Chua-anusorn, K.C. Tran, J. Webb, D.J. Macey, T.G. St Pierre

Inorg. Chim. Acta 300–302 (2000) 932

Chemical speciation of iron deposits in thalassemic heart tissue

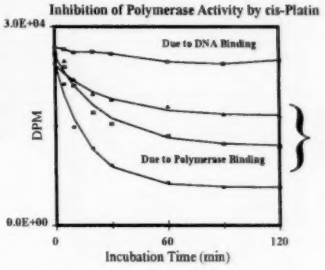
Mössbauer spectroscopy of β-thalassemia/hemoglobin E heart tissue and ferritin and hemosiderin indicated that approximately 40% of the tissue iron is in the form of poorly crystalline hemosiderin, 35% in the form of ferritin with ferrihydrite cores, 3% in the form of heme iron, and approximately 20% in the form of an unidentified form of paramagentic iron.

Rathindra N. Bose, Kristi Allen, Michael Wagner, Erika Volckova, Dawei Li, Robert T. Heath

Inorg. Chim. Acta 300–302 (2000) 937

DNA polymerase versus DNA binding to the anticancer drug, *cis*-platin

Inhibition of the polymerase activity of *E. coli* polymerase I by *cis*-platin is due primarily to platination to the Klenow fragment of the enzyme, but not to DNA. Competition reactions of *cis*-platin with a mixture of peptide, selected from human DNA polymerase-α, and 5′-GMP support preferential binding to enzyme over DNA.

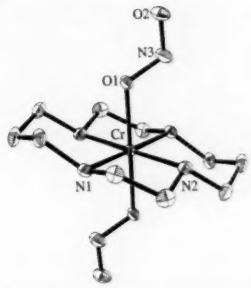


Malcolm A. De Leo, Xianhui Bu, Jason Bentow, Peter C. Ford

Inorg. Chim. Acta 300–302 (2000) 944

The synthesis, characterization and structures of the chromium(III) dinitrito complexes: *trans*-$[Cr(L)(ONO)_2]^+$ (L = 1,4,8,11-tetraazacyclotetradecane or 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)

The syntheses, spectroscopy and structures of the Cr(III) complexes *trans*-$[Cr(cyclam)(ONO)_2](BF_4)$ (**1**) and $[Cr(tetA)(ONO)_2](NO_3)\cdot H_2O$ (**2**) are described. The optical spectra are dominated by a ligand field band at 476 and 480 nm and by a nitrite localized $n-\pi^*$ band at 336 and 344 nm, respectively. These compounds undergo NO photodissociation when irradiated with near UV or visible light.

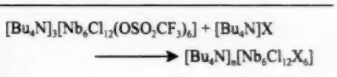


Nicholas Prokopuk, Charles S. Weinert, Vance O. Kennedy, David P. Siska, Hee-Joo Jeon, Charlotte L. Stern, Duward F. Shriver

Inorg. Chim. Acta 300–302 (2000) 951

Synthesis and structure of the useful starting material $[Bu_4N]_3[Nb_6Cl_{12}(OSO_2CF_3)_6]$

The cluster $[Bu_4N]_3[Nb_6Cl_{12}(OSO_2CF_3)_6]$ (**1**) has been prepared by reaction of methyl triflate ($CH_3OSO_2CF_3$) with the all-chloro cluster $[Bu_4N]_3[Nb_6Cl_{12}Cl_6]$. This material has been characterized by IR and UV–Vis spectroscopy, cyclic voltammetry, and X-ray crystallography. This material has been used to prepare the clusters $[Bu_4N]_n[Nb_6Cl_{12}X_6]$ (X = Cl, Br, I; $n = 3$; X = NCS, $n = 4$). These products have been characterized by elemental analysis and cyclic voltammetry.

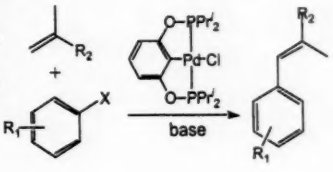


David Morales-Morales, Christian Grause, Kristie Kasaoka, Rocío Redón, Roger E. Cramer, Craig M. Jensen

Inorg. Chim. Acta 300–302 (2000) 958

Highly efficient and regioselective production of trisubstituted alkenes through heck couplings catalyzed by a palladium phosphinito PCP pincer complex

The novel palladium phosphinto PCP pincer complex, $PdCl\{C_6H_3\text{-}2,6\text{-}(OPPr^i_2)_2\}$ is a highly efficient catalyst for the olefination of aryl brmides and iodidies under aerobic conditions. Most significantly, one isomer of trisubstituted alkenes can be produced in ≥ 90% yield from the Heck coupling of 1,1 disubstituted alkenes and bromobenzenes.

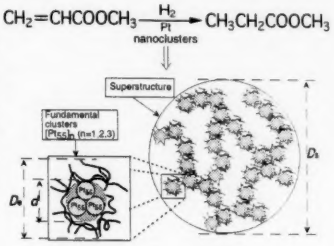


Yukihide Shiraishi, Masako Nakayama, Etsuko Takagi, Toshihiro Tominaga, Naoki Toshima

Inorg. Chim. Acta 300–302 (2000) 964

Effect of quantity of polymer on catalysis and superstructure size of polymer-protected Pt nanoclusters

The poly(*N*-vinyl-2-pyrrolidone) (PVP)-protected Pt nanoclusters, prepared at various mole ratios of PVP to Pt, were characterized by transmission electron microscopy, atomic force microscopy and the Taylor dispersion method. Hydrogenation of methyl acrylate in ethanol was used for evaluation of the catalytic activities, suggesting that the catalytic activity of Pt nanoclusters depends on the superstructure size of Pt nanoclusters protected by PVP.

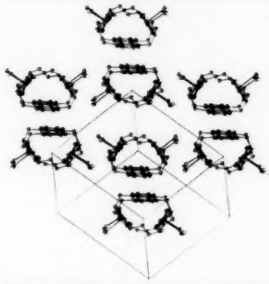


M. Isabel Burguete, Beatriz Escuder, Enrique García-España, Julio Latorre, Santiago V. Luis, José Antonio Ramírez

Inorg. Chim. Acta 300–302 (2000) 970

New strategies in the development of polynuclear complexes. Crystal structure of the tetranuclear copper(II) complex $[Cu_4(\mathbf{L1})_2(OH)_4Cl_2(H_2O)_2]_2$-$(H_3O_2)(ClO_4)_2Cl{\cdot}2H_2O$ (**L1** = 2,5,8,11-tetraaza[12]-(1,4)naphthalenecyclophane)

The preparation and interaction of the new polyaza[n]naphthalenophanes 2,5,8, 11-tetraaza[12](1,4)naphthalenophane and 2,6,9,13 - tetraaza [14] (1,4) naphthalenophane with hydrogen ions and Cu^{2+} is described.

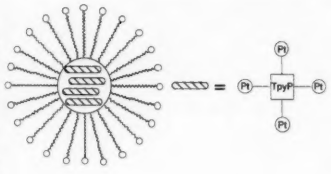


Luigi Monsú Scolaro, Caterina Donato, Mariangela Castriciano, Andrea Romeo, Raffaello Romeo

Inorg. Chim. Acta 300–302 (2000) 978

Micellar aggregates of platinum(II) complexes containing porphyrins

A tetranuclear cationic platinum(II) complex containing TpyP porphyrin interacts with aqueous micellar phases aggregating in the hydrophobic region of anionic SDS and neutral TX-100 micelles. Experimental findings also suggest partial intercalation in the hydrophilic area of neutral micelles. Formation of premicellar aggregates with SDS has been evidenced. The metalated Mn(III) porphyrin derivative exhibits a moderate peroxidase activity.

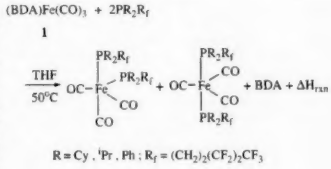


Dale C. Smith, Amy L. Klaman, Jérémie Cadoret, Steven P. Nolan

Inorg. Chim. Acta 300–302 (2000) 987

Synthetic and thermochemical studies of fluorinated tertiary phosphine ligands R_2PR_f [R = Cy, Ph, ^{i}Pr; $R_f = CH_2CH_2(CF_2)_5CF_3$] in an organoiron system

The fluorinated phosphine ligands $[PR_2R_f$ (R = Cy (**2**); ^{i}Pr, (**3**); Ph, (**4**); R_f = $CH_2CH_2(CF_2)_5CF_3]$ react with $Fe(CO)_3$-(BDA) (**1**) (BDA = $(C_6H_5)CH{=}CHC$-$(O)CH_3$, benzylideneacetone) to yield the corresponding $Fe(CO)_3(PR_2R_f)_2$ (R = Cy, (**5**) ^{i}Pr, (**6**) Ph, (**7**)) complexes. Infrared studies on the carbonyl complexes and solution calorimetry studies of the reaction of **1** with **2**, **3** and **4** have been performed to quantify the donor strength of this series of ligands.

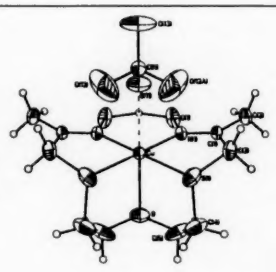


Michael J. Prushan, Anthony W. Addison, Raymond J. Butcher

Inorg. Chim. Acta 300–302 (2000) 992

Pentadentate thioether-oxime macrocyclic and quasi-macrocyclic complexes of copper(II) and nickel(II)

Several pentadentate thioether-oxime ligands and their respective Cu(II) and Ni(II) complexes were synthesized. Macrocyclization was achieved by reaction with either BF_2^+ or in the case of the Cu(II) complexes reaction with BF_4^-. The complexes were characterized by X-ray crystallography, UV–Vis, ESR spectrometry and electrochemical methods. The ligands with N_2S_3 donor sets stabilize both Ni(III) and Ni(I) whereas the Cu(II) complexes stabilize only Cu(I).

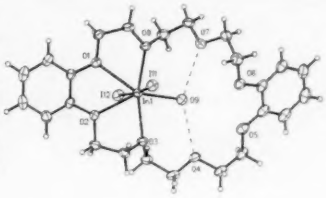


Gerald R. Willey, Damian R. Aris, William Errington

Inorg. Chim. Acta 300–302 (2000) 1004

Crown ether complexation of p-block metal halides: synthesis and structural characterisation of $[InI_2(dibenzo\text{-}24\text{-}crown\text{-}8)(H_2O)][InI_4]$, $[(SnBr_4)_2(dibenzo\text{-}24\text{-}crown\text{-}8)]MeCN$, $[(SbCl_3)_2(dibenzo\text{-}24\text{-}crown\text{-}8)]MeCN$, $[(BiCl_3)_2(dibenzo\text{-}24\text{-}crown\text{-}8)]MeCN$ and $[(SbBr_3)_2(dibenzo\text{-}24\text{-}crown\text{-}8)]$

Complexes of dibenzo-24-crown-8 with In(III), Sn(III), Sb(III) and Bi(III) halides have been isolated and structurally characterised. All are dinuclear except the In(III) species (auto-ionised). The location of the metal centres with respect to the ring cavity varies between *direct encapsulation* (In(III)), *peripheral* (Sb(III) and Bi(III)) and *exocyclic* (Sn(IV)).

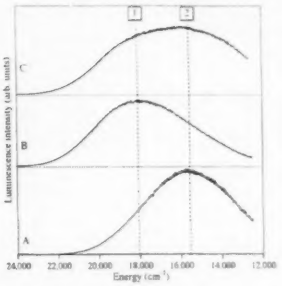


Sachio Murakami, Markus Herren, Doris Rau, Makoto Morita

Inorg. Chim. Acta 300–302 (2000) 1014

Photoluminescence and decay profiles of undoped and Fe^{3+}, Eu^{3+}-doped PLZT ceramics at low temperatures down to 10 K

Luminescence, time-resolved luminescence, excitation spectra and lifetimes of nominally pure and Eu, Fe-doped (Pb, La) (Zr, Ti) O_3 (PLZT) ceramics are investigated at low temperatures down to 10 K. Luminescence centers in hot-/cold-pressed PLZT (9/65/35) and cold-pressed PLZT (8/70/30) consist of two bands which are due to $[Ti(IV)O_6]$ and $[Fe(III)O_{6-\delta}]$ structures.

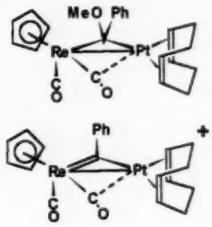


Mirka Bergamo, Tiziana Beringhelli, Giuseppe D'Alfonso, Pierluigi Mercandelli, Massimo Moret, Angelo Sironi

Inorg. Chim. Acta 300–302 (2000) 1022

Solid state and solution structure of the heterodimetallic complexes $[Cp(CO)_2Re\{\mu\text{-}C(OMe)(Ph)\}Pt(COD)]$ and $[Cp(CO)_2Re\{\mu\text{-}CPh\}Pt(COD)]^+$, containing bridging carbene and carbyne ligands

Reaction of $[Cp(CO)_2Re{=}C(OMe)(Ph)]$ with $[Pt(COD)_2]$ affords the novel complex $[Cp(CO)_2Re\{\mu\text{-}C(OMe)(Ph)\}Pt(COD)]$, containing a bridging carbene. Its reaction with $(Me_3O)BF_4$ results in the formation of the carbyne-bridged $[Cp(CO)_2Re\{\mu\text{-}CPh\}Pt(COD)]^+$ cation. The two complexes represent the highest members, as far as the Pt:Re ratio is concerned, of the small family of phosphorous-free Pt–Re mixed metal complexes containing Pt–Re bonds.

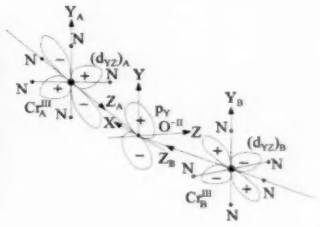


Claus E. Schäffer

Inorg. Chim. Acta 300–302 (2000) 1035

Extension of ligand-field theory to encompass bridged structures. Emphasis on the angular overlap model

Non-linear ligation and pathways for superexchange are parameterized in the angular overlap model. From a point on the virtual interface between the central ion and ligand spheres, both containing an integral number of electrons, the molecular orbital angular overlap model (MO-AOM) sees and quantifies all the symmetry relationships between the atomic orbitals of the two spheres and mimics MO theory.



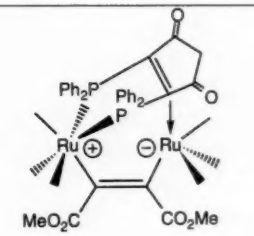
Notes

Simon G. Bott, Huafeng Shen, Michael G. Richmond

Inorg. Chim. Acta 300–302 (2000) 1077

Photochemically mediated alkyne metalation in the donor–acceptor complexes $Ru_2(CO)_6(\mu\text{-P–P})$ [where P–P = bpcd, (Z)-$Ph_2PCH{=}CHPPh_2$]. X-ray diffraction structure of the zwitterionic compound $Ru_2(CO)_6[\mu\text{-}(Z)\text{-}MeO_2CC{=}CO_2Me](\mu\text{-bpcd})$

Near-UV irradiation of the donor–acceptor complexes $Ru_2(CO)_6(\mu\text{-bpcd})$ and $Ru_2(CO)_6[\mu\text{-}(Z)\text{-}Ph_2PCH{=}CHPPh_2]$ in the presence of dimethyl acetylenedicarboxylate (dmad) gives the dimetalated alkene complexes $Ru_2(CO)_6[\mu\text{-}(Z)\text{-}MeO_2CC{=}CCO_2Me](\mu\text{-diphosphine})$. Each new alkene complex was characterized in solution and by X-ray diffraction analysis in the case of the bpcd-substituted derivative. The X-ray structure of $Ru_2(CO)_6[\mu\text{-}(Z)\text{-}MeO_2CC{=}CCO_2Me](\mu\text{-bpcd})$ confirms the formal oxidative addition of the dmad ligand across the dative Ru–Ru bond.

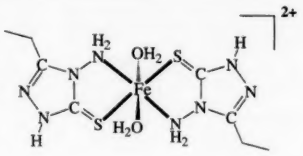


Todd W. Kajdan, Philip J. Squattrito, Surendra N. Dubey

Inorg. Chim. Acta 300–302 (2000) 1082

Coordination geometries of bis(4-amino-3-ethyl-1,2,4-triazole-5-thione) complexes of Mn, Fe, Co, Ni, Cu and Zn: relationship to the 3-methyl analogs

The chelating ligand 4-amino-3-ethyl-1,2,4-triazole-5-thione (aet) has been used to form a series of bis bidentate complexes with divalent Mn, Fe, Co, Ni, Cu, and Zn. The complexes contain two water molecules to complete the octahedral coordination sphere, except for Cu which coordinates nitrate anions. Different coordination geometries were observed based on the identities of the metal ions. For $[M(aet)_2(H_2O)_2](NO_3)_2$, the Mn complex has a *cis* geometry, while the isostructural Co, Ni and Zn complexes display a *trans* arrangement as does the complex in $[Fe(aet)_2(H_2O)_2](ClO_4)_2 \cdot 2H_2O$. The copper complex $[Cu(aet)_2(NO_3)_2]$ has a Jahn–Teller distorted octahedral geometry with two more distant nitrate O atoms. These results are compared with those of the analogous complexes of 4-amino-3-methyl-1,2,4-triazole-5-thione.

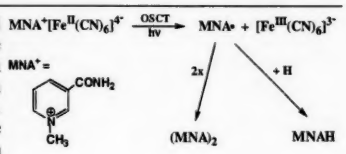


Horst Kunkely, Arnd Vogler

Inorg. Chim. Acta 300–302 (2000) 1090

Photochemical reduction of 1-methyl-3-carbamoyl-pyridinium by hexacyanoferrate(II) induced by outer-sphere charge transfer excitation

The NAD^+ subunit 1-methyl-3-carbamoyl pyridinium cation (or 1-methyl nicotinamide cation, MNA^+) forms an ion pair with $[Fe(CN)_6]^{4-}$ which shows a new absorption ($\lambda_{max} = 392$ nm) in the electronic spectrum. This band is assigned to an outer-sphere charge transfer (OSCT) transition from $[Fe(CN)_6]^{4-}$ to MNA^+. In aqueous solution OSCT excitation leads to a photoredox reaction with the formation of $[Fe(CN)_6]^{3-}$ and the radical $MNA^\bullet$ which undergoes a dimerization or, more likely, a further reduction to MNAH.

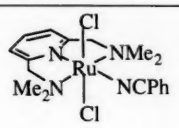


Ignacio del Río, Stephan Back, Milja S. Hannu, Gerd Rheinwald, Heinrich Lang, Gerard van Koten

Inorg. Chim. Acta 300–302 (2000) 1094

Reactivity of the binuclear ruthenium 'Pincer' complex $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ towards N-donor ligands. The X-ray crystal structure of $[RuCl_2(\eta^3\text{-}NN'N)(NCPh)]$ ($NN'N$ = 2,6-bis[(dimethylamino)methyl]pyridine)

The dinitrogen-bridged complex $\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)$ ($NN'N$ is neutral $C_5H_3\text{–}N(CH_2NMe_2)_2\text{-}2,6$) reacts with 2 equiv. of MeCN to *mer,trans*-$[RuCl_2(\eta^3\text{-}NN'N)(NCMe)]$, while excess MeCN provides the monocationic *mer,cis* and *mer,trans* - $RuCl_2(\eta^3\text{ - }NN'N)(NCMe)_2]Cl$. Reaction with excess PhCN or pyridine gives exclusively the neutral *mer,trans*-complexes $[RuCl_2(\eta^3\text{-}NN'N)(L)]$ (L = PhCN or py). An X-ray of the complex with L = PhCN is also reported.

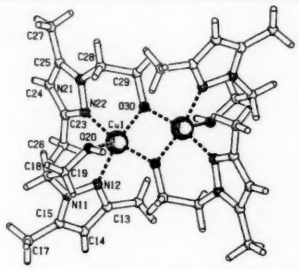


Willem L. Driessen, Bas Maase, Jan Reedijk, Huub Kooijman, Miles T. Lakin, Anthony L. Spek

Inorg. Chim. Acta 300–302 (2000) 1099

A dinuclear copper(II) and a mononuclear cobalt(II) compound of the didentate *N,O*-donor ligand 1-(2-hydroxyethyl)-3,5-dimethylpyrazole

The didentate *N,O*-donor ligand 1-(2-hydroxyethyl)-3,5-dimethylpyrazole can bind metal ions both in the neutral form and after dehydronation, analogous to amino alcohols.

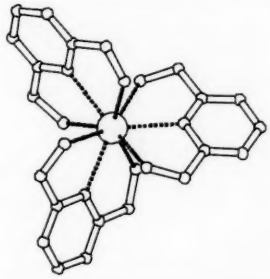


Dave R. van Staveren, Gerard A. van Albada, Syb Gorter, Jaap G. Haasnoot, Jan Reedijk

Inorg. Chim. Acta 300–302 (2000) 1104

Synthesis, characterization and luminescence properties of lanthanide(III) compounds with 2,6-di(hydroxymethyl)pyridine and the related 2,6-di(hydroxymethyl-d_2)pyridine ligand. X-ray structure of $[Sm(2,6\text{-di(hydroxymethyl)pyridine})_3](NO_3)_3$

Luminescence lifetime experiments of Eu^{3+} in solution are described, together with a Sm^{3+} crystal structure in the solid phase.

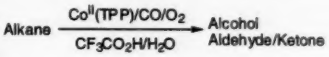


Hui Tang, Chengyu Shen, Minren Lin, Ayusman Sen

Inorg. Chim. Acta 300–302 (2000) 1109

Cobalt porphyrin-catalyzed alkane oxidations using dioxygen as oxidant

In a mixture of trifluoroacetic acid and water, cobalt(II) porphyrin complexes catalyze the oxidation of alkanes by dioxygen. Carbon monoxide is required as a coreductant for the oxidations to proceed. While the turnover rates are slow, the system displays unusual selectivity in that primary C–H bonds are more reactive than the weaker secondary C–H bonds or C–H bonds α to an alcohol functionality.



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